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Zinc–zinc bonded decamethyldizincocene $\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2$ as catalyst for the inter- and intramolecular hydroamination reaction†Anja Lühl,^a Hari Pada Nayek,^a Siegfried Blechert^{*b} and Peter W. Roesky^{*a}

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The Zn–Zn bonded compound $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ was investigated as catalyst for the inter- and intramolecular hydroamination reaction. High reaction rates under mild conditions were observed. This is the first application of a Zn–Zn bonded compound as catalyst.

The landmark discovery of the Zn–Zn bonded decamethyldizincocene $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) by Carmona *et al.*¹ was the beginning of a broad chemistry dealing with the synthesis and reactivity of low-valent metal–metal bonded organozinc compounds.² Besides investigations on the nature of the Zn–Zn bond³ a number of low-valent dizinc compounds with the general formula R_2Zn_2 ($\text{R} = \text{EtMe}_4\text{C}_5$,^{1b} $[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{Me})\text{C}]_2\text{CH}$],⁴ $[2,6\text{-}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{C}_6\text{H}_3]$,⁵ $[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{N}(\text{Me})\text{C}]_2$,⁶ $[(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\text{NCH}]_2$,^{6a} $[\text{Me}_2\text{Si}\{\text{N}(2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)\}_2]$,⁷ $[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{N}(\text{Me})\text{C}]_2\text{CH}$],⁸ 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene,⁹ bis(phosphinimino)methanides,¹⁰ tris(3,5-dimethylpyrazolyl)hydridoborate,¹¹ and aminotroponimines¹² have been synthesized. Recently some groups have started to study the reactivity of $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ with H_2O , $t\text{-BuOH}$, and NCXyl resulting in the formation of elemental zinc and the corresponding $\text{Zn}(\text{II})$ complexes through disproportionation.¹ Very recently, Schulz *et al.* reported on the reaction of $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ with the strong Lewis base 4-(dimethylamino)pyridine (dmap) giving the first Lewis acid–base adduct of dizincocene $[(\eta^5\text{-Cp}^*)\text{Zn}\text{-Zn}(\text{dmap})_2(\eta^5\text{-Cp}^*)]$.¹³ Further reaction with $[\text{H}(\text{OEt})_2][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ resulted in the base-stabilized $[\text{Zn}_2]^{2+}$ cation $[\text{Zn}_2(\text{dmap})_6][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]_2$.¹³ A similar protonation reaction of $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ with various nitrogen based ligands (L)^{10,12} resulted in the Zn–Zn-bonded complexes $[(\text{L})_2\text{Zn}_2]$ upon elimination of Cp^*H .⁸ Carmona *et al.* revealed the synthesis of $[(\eta^5\text{-Cp}^*)(\text{OR})(\text{L})_x\text{Zn}_2]$ ($\text{R} = 2,6\text{-}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{C}_6\text{H}_3$ and Cp^* ; $\text{L} = 4\text{-pyrrolidinopyridine}$).¹⁴ To the best of our

knowledge, there have no catalytic applications of any of these Zn–Zn bonded compounds been reported so far.

We have explored for some time now the catalytic potential of various zinc alkyl species for the hydroamination reaction.¹⁵ Hydroamination is the formal addition of an organic amine N–H bond to an unsaturated carbon–carbon bond in one step to give nitrogen containing molecules.¹⁶ The catalytic version of this reaction is of great interest for academic and industrial research because nowadays most amines are made in multi-step syntheses. Zinc complexes as catalysts for hydroamination reaction possess several advantages in comparison to the well established catalysts: They show a high tolerance towards polar functional groups and some of them are relatively stable towards air and moisture. Furthermore, zinc is an inexpensive and non-toxic metal which makes its use in catalysis attractive.

Herein we report on the application of the Zn–Zn bonded complex $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ as catalyst for the inter- and intramolecular hydroamination reactions with different functional groups on the substrates (Table 1–2). Although some reactions were already run at room temperature most of the reactions were carried out at 80 °C in benzene with a catalyst loading of 2.5 mol%, 2.5 mol% of $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ as a cocatalyst and ferrocene as internal standard. It was shown earlier by us that the addition of one equivalent of $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ has a beneficial effect on the reactivity of the zinc catalyst. We anticipate the formation of a cationic zinc species which is formed by the protonolysis of the Cp^* moiety because Cp^*H could be detected in the NMR spectrum as byproduct. We also tested both compounds separately in the reaction of phenylethyne with anilines (Table 2, entry 1). The cocatalyst alone did not catalyze the reaction at all under the described conditions. By using $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ without cocatalyst only polymers were obtained.

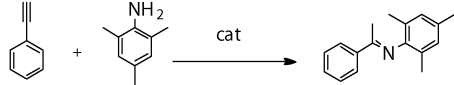
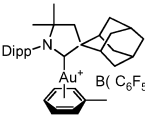
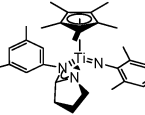
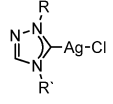
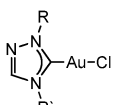
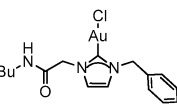
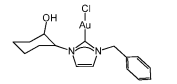
First, we compared the catalytic potential of $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ with published systems in the intermolecular hydroamination reaction. We used the addition of 2,4,6-trimethylaniline to phenylethyne as a standard reaction because this reaction has also been studied with many other reported catalysts (Table 1).¹⁷ Although a titanium catalyst is shown in Table 1 (entry 3), most reported catalysts for this reaction are based on Group 11 metals. $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ (Table 1, entry 1) is the only catalyst that catalyzes the transformation at room temperature, whereas most of the other systems operate in the range of 90–110 °C (Table 1, entries 3–6 and 8–11). With typical catalyst and cocatalyst loading of 2.5 mol% each the isolated yield was 99% for this catalytic

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† Electronic supplementary information (ESI) available: Table S11, Kinetic Studies and NMR spectra. See DOI: 10.1039/c1cc12461g

Table 1 Intermolecular hydroamination of phenylethyne with 2,4,6-trimethylaniline

						
Entry/ Ref.	Cat.	T [°C]	t [h]	Yield [%]	Mol% cat.	Ratio amine/ alkyne
1	[(η ⁵ -Cp*) ₂ Zn ₂]	23	11.25	Quant. (NMR)	2.5	1:1
		23	5.5	Quant. (NMR)	2.5	1:2
2 ^{17a}		40	16	81 (NMR)	5	1:1
3 ^{17b}		105	24	80 (isolated)	5	1:1
4 ^{17c}	CuSTA ^a	110	4	75 (GC)		2:1
			8	95 (GC)		2:1
5 ^{17d}	CuA1SBA-15	110	6	37		2:1
6 ^{17e}	Cu-K-10 ^b	110	20	95 (GC)	10 wt (%)	2:1
			20	91 (isolated)		
7 ^{17f}	(Ph ₃ P)AuCH ₃ + H ₃ PW ₁₂ O ₄₀	70	2	93 (NMR)	0.2:1	1.1:1
8 ^{17f}						
		R = CH ₂ CO ₂ Bu, R' = CH ₂ Ph (I)	90	7		
		R = CH ₂ CONH ₂ Bu, R' = CH ₂ Ph (II)	90	0		
			12		2	1:1.5
		R = CH ₂ CO ₂ Bu, R' = CH ₂ CO ₂ Bu (III)	90	16		
		R = C ₆ H ₁₀ OH, R' = CH ₂ Ph (IV)	90	1		
9 ^{17f}						
		R = CH ₂ CO ₂ Bu, R' = CH ₂ Ph (V)	90	84		
		R = CH ₂ CONH ₂ Bu, R' = CH ₂ Ph (VI)	90	75		
			12		2	1:1.5
		R = CH ₂ CO ₂ Bu, R' = CH ₂ CO ₂ Bu (VII)	90	80		
		R = C ₆ H ₁₀ OH, R' = CH ₂ Ph (VIII)	90	58		
10 ^{17f}		90	12	16	2	1:1.5
11 ^{17f}		90	12	46	2	1:1.5

^a Copper salt of silicotungstic acid; ^b montmorillonite K-10.

reaction (Table 2, entry 1E). Although the reaction temperature for [(η⁵-Cp*)₂Zn₂] was significant lower, the time needed for a full conversion is comparable to the other catalysts. Therefore, [(η⁵-Cp*)₂Zn₂] is the most active system in the series shown in Table 1 for the standard reaction. Surprisingly, even some sophisticated gold and silver catalysts (Table 1, entries 2 and 8–11) could not compete. The reaction rate of [(η⁵-Cp*)₂Zn₂] could even be further increased by applying an amine to alkyne ratio of 1:2.



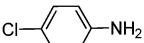
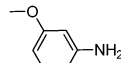

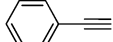
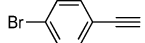
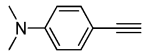
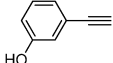
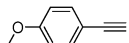
Recently the hydroamination of phenylethyne with aniline catalyzed by Zn(OTf)₂ followed by a reduction was reported.¹⁸ Although our yield is a bit lower (89% vs. 98% for Zn(OTf)₂) [(η⁵-Cp*)₂Zn₂] catalyzes this reaction in shorter time (15h vs. 24h) at lower reaction temperature (80 °C vs. 120 °C) with half of the catalyst loading (Fig. S1†).

As shown in Table 2 we then investigated various intermolecular hydroamination reactions by using substituted primary and secondary anilines with different functional groups and different arylethyne. In this screening we used an amine to alkyne ratio of 1:1, since we aimed to have full conversion without any by-product or starting material. Quantitative Markovnikov regio-selectivity was observed for all reactions shown in Table 2. As functional groups halides, methoxy, and even OH were tolerated. The reactions were run in benzene at 80 °C with the exception of 2,4,6-trimethylaniline (Table 2, entry E) and some reactions of 3-methoxyaniline (Table 2, entry 3D), which already reacted in acceptable rates at room temperature. With a few exceptions all reactions run with a conversion of 90%–100%. In general the reactions of the secondary aniline diphenylamine did not proceed whereas the reaction of *N*-methylaniline gave lower yields with 4-ethynyl-dimethylaniline, 3-ethynylphenol, and 1-ethynyl-4-methoxybenzene (Table 2, entries 3B–5B). Kinetic investigations have shown a substrate dependence of the rate. For the standard reaction (addition of 2,4,6-trimethylaniline to phenylethyne) a zero order kinetic was observed for the first 90% of conversion (Fig. S2†). The steric demand of the aniline has no influence on the reaction rate. In contrast, the addition of 3-methoxyaniline to 4-ethynyl-dimethylaniline (Table 2, entry 3D) is more complicated and no clear rate law could be assigned (Fig. S3†). Nevertheless, both kinetic measurements show neither any induction period nor an unstable conversion. Obviously a stable catalytic species is formed *in situ* but in the present stage we do not know the exact nature and the oxidation state of the catalytic active species.

Finally, we investigated the catalytic activity of [(η⁵-Cp*)₂Zn₂] in the intramolecular hydroamination reaction. Surprisingly the incorporation of functional groups (Table SII†, entries 1–2) did not have a significant influence on the conversion. All intramolecular cyclizations of secondary amino olefins were completed in 10–40 min in quantitative yields. In contrast, the cyclization of a primary amino alkyne went much slower (Table SII†, entry 4). Beside the imine, the corresponding enamine was obtained as a byproduct.

In conclusion, we have shown the first application of a Zn–Zn bonded compound as a catalyst. [(η⁵-Cp*)₂Zn₂] can be applied as a homogenous catalyst for the intra- and intermolecular hydroamination reaction in the presence of equimolar amounts of [PhNMe₂H][B(C₆F₅)₄]. Many functional groups are tolerated. The addition of 2,4,6-trimethylaniline to phenylethyne catalyzed

Table 2 Intermolecular hydroamination of anilines and alkynes catalyzed by $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]^a$

Entry	Substrates	<div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;">  A </div> <div style="text-align: center;">  B </div> <div style="text-align: center;">  C </div> <div style="text-align: center;">  D </div> <div style="text-align: center;">  E </div> </div>				
1		9 h, 95%	3.5 h, 82%	5 h, 87%. (22% bypr) ^c	18 h, 89% (6% bypr) ^c 36 h, 93%. (7% bypr) ^c	11.25 h, Quant. ^d 99% ^{b,d}
2		9 h, 96%	15 h, 99%	4 h, 88%; 10 h, Quant.	18 h, 75% 48 h, 93%	19.66 h, 93% ^d 21.66 h, 95% ^d
3		5 h, Quant.	1 h, 20%	5 h, Quant.	25 h, 93% ^d 48 h, 99% ^d	19.75 h, 93% ^d 21.75 h, 96% ^d
4		6.5 h, 82% 30 h, 97%	— ^e	34 h, 99%	9 h, 41% 5 h, 38%	41.75 h, 69% ^d 43.75 h, 70% ^d
5		8 h, Quant. (4% bypr) ^c	3 h, 71%	5 h, 92% (8% bypr) ^c	9 h, 97%	— ^e

^a Reagents and conditions: substrate (0.5 mmol), catalyst (2.5 mol%), $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ (2.5 mol%), C_6D_6 , 80 °C, conversion determined by ¹H NMR; ^b isolated yield; ^c bypr = byproduct: the corresponding enamine; ^d reaction at room temperature; ^e no conversion.

by $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ proceeds already at room temperature. Thus, for this reaction $[(\eta^5\text{-Cp}^*)_2\text{Zn}_2]$ is more active than any other catalyst.

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