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β-Diketiminate Zinc Complexes for the Hydroamination of Alkynes

Mustafa Biyikal,[a] Karolin Löhnwitz,[b] Nils Meyer,[c] Maximilian Dochnahl,[a][‡]
Peter W. Roesky,*[b] and Siegfried Blechert*[a]

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A series of electronically and sterically modified β-diketiminate methylzinc complexes [{*N*,*N*′-bis(2,6-diisopropylphenyl)-β-diketiminato}methylzinc] (**1**), [{*N*,*N*′-bis(2-isopropylphenyl)-β-diketiminato}methylzinc] (**2**), [{*N*,*N*′-bis(2,4,6-trimethylphenyl)-β-diketiminato}methylzinc] (**3**), [{*N*,*N*′-bis(4-methoxyphenyl)-β-diketiminato}methylzinc] (**4**), a bis(β-diketiminato)zinc compound [bis{*N*,*N*′-bis(4-methoxyphenyl)-β-diketiminato}zinc] (**5**), and a β-diketiminate bis(trimethylsilylamido)zinc complex [{2-(1-cyclohexylimidazolidine-2-ylidene)-1-methylethylidene-(2,6-diisopropylphenyl)aminato}-bis(trimethysilylamido)zinc] (**6**) were prepared and structurally characterized by single-crystal X-ray diffraction. All methylzinc compounds exhibit a trigonal-planar coordinated zinc atom, with the exception of polymeric compound **4**, in which intermolecular coordination of the OMe group to the zinc atom additionally takes place. All zinc complexes were investigated as catalysts in the intramolecular hydroamination of nonactivated alkynes and show high catalytic activity in the presence of the cocatalyst [$PhNMe_2H$][SO_3CF_3]. The zinc complex **1** shows the highest catalytic activity in most of the cyclization reactions. In this context, it was possible to isolate the intermediate, which was formed by the reaction of the precatalyst **1** and the cocatalyst [$PhNMe_2H$][SO_3CF_3]. The resulting zinc catalyst [{*N*,*N*′-bis(2,6-diisopropylphenyl)-β-diketiminato}(trifluoromethanesulfonate)zinc]·thf (**7**) was structurally characterized by single-crystal X-ray diffraction. The zinc complex **7** show the same catalytic activity in the hydroamination when an equimolar mixture of the precatalyst **1** and the cocatalyst was used. It is supposed that the high steric bulk of the precatalyst **1** protects the Lewis acid zinc center from polar functional groups but allows interactions for the cyclization process.

Introduction

The catalytic addition of organic amine N–H bonds to multiple C–C bonds is a powerful and atom-economical method for the synthesis of nitrogen-containing molecules. Hydroamination has been studied extensively with various metal catalysts. The widespread search for homogeneous catalysts for this process has begat a burgeoning and mechanistically diverse area of research that has utilised lithium,[1] group 4 metals,[2] the lanthanides,[3–6] the platinum metals,[7] the alkaline earth metals,[8] copper,[9] silver,[10] and gold.[11] The scope of catalytic hydroamination reactions has been reviewed recently.[12,13] The lanthanides are especially highly efficient catalysts for the hydroamination of various multiple bonds, but they display limited functional group tolerance and high air- and moisture sensitivity, which makes their routine preparation and application in synthesis problematic. Unlike the early transition metals, the late transition metals have a much higher tolerance towards water, oxygen impurities, and functional groups. Therefore, they have a broader potential for application in organic synthesis. Most of these catalysts are based on relatively expensive gold, palladium, platinum, or on nickel. Moreover, for nonactivated substrates, most of the late-transition-metal catalysts show limited scope, modest selectivity, and sluggish reaction rates.

Organozinc complexes are extensively used in organic syntheses.[14] We developed aminotroponiminate methylzinc complexes as catalysts for intramolecular hydroamination.[15–17] In this context, we investigated the influence of steric modifications of the alkyl groups at the nitrogen atoms of the aminotroponimine ligand and of electronic modifications by using aminotroponiminates having a phenylsulfanyl in 5-position of the ligand. We were able to show the major influence of the steric and electronic environment around the zinc atom on both the reactivity and stability of the corresponding complexes.[17] The resulting zinc complexes possess interesting advantages relative to other metal catalysts such as (i) they show a very high tolerance towards polar functional groups and (ii) they are remarkably stable towards air and moisture. So far, we focused on aminotroponiminate zinc complexes. Herein, we

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[a] Institut für Chemie, Technische Universität Berlin,
Strasse des 17. Juni 115, 10623 Berlin, Germany
Fax: +49-30-3142-3619
E-mail: blechert@chem.tu-berlin.de
[b] Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT),
Engesserstr.15, 76128 Karlsruhe, Germany
Fax: +49-721-608-4854
E-mail: roesky@kit.edu
[c] Institut für Chemie und Biochemie, Freie Universität Berlin,
Fabeckstrasse 34-36, 14195 Berlin, Germany
[‡] Present address: BASF SE, Global Research Crop Protection,
67056 Ludwigshafen, Germany

report on β-diketiminate (BDI) zinc complexes as catalysts for intramolecular hydroamination. Even though β-diketiminate complexes of cobalt, nickel, copper and zinc are known since the late 1960s,[18–20] the first catalytic applications were reported as late as the 1990s.[21–26] Coates et al. have demonstrated that zinc alkoxides with bulky β-diketiminate ligands in the coordination sphere show very high rates for the (living) copolymerization of cyclohexene oxide and CO_2 to make polycarbonates,[27–30] the synthesis of poly(lactic acid) by stereoselective ROP of lactide,[31,32] and the ring-opening polymerization of β-butyrolactone and γ-valerolactone.[33] Rieger et al. have shown that the ethylsulfinate ligand is a highly efficient initiating group for the β-diketiminate-zinc-catalyzed copolymerization reaction of CO_2 and epoxides.[34,35]

Herein we report the synthesis of six β-diketiminate zinc complexes (compounds **2**–**7**; Figure 1, Schemes 3 and 4) including the novel type of an imidazoline version **6** and their application as catalysts for the hydroamination of nonactivated alkynes.

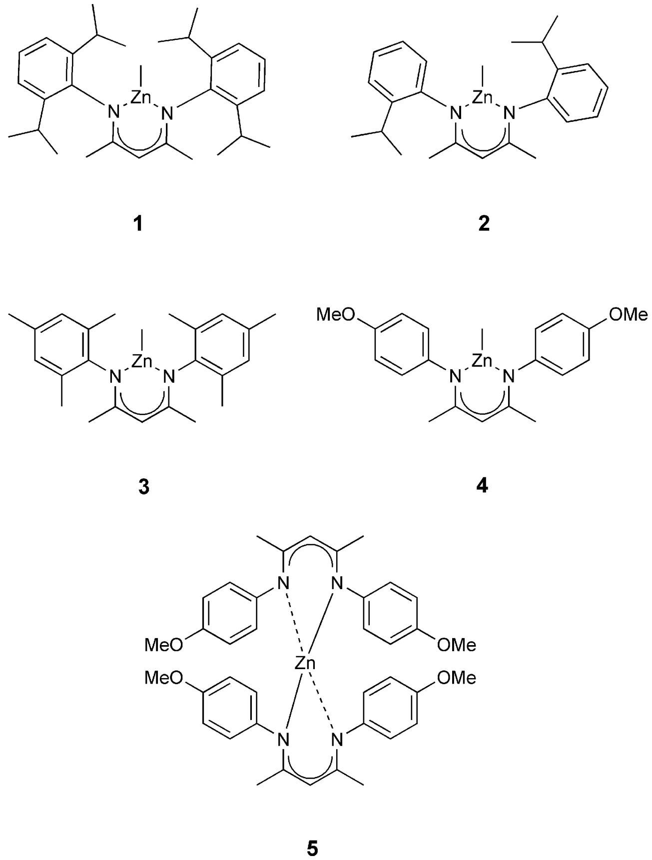


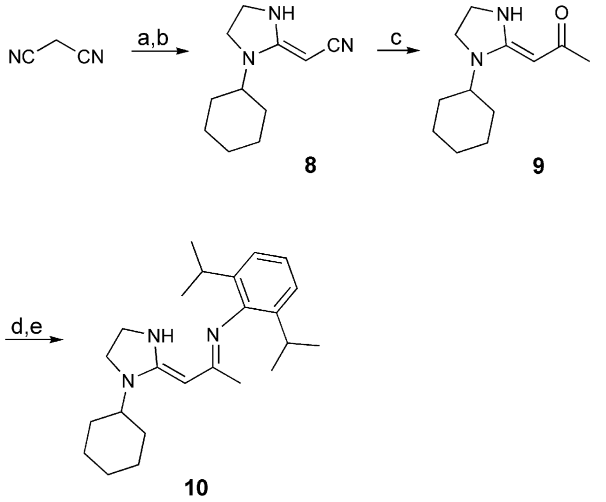
Figure 1. Structure of the β-diketiminate zinc complexes **1**–**5**.

Results and Discussion

Ligand Synthesis

Several synthetic routes to β-diketimine ligands have been reported.[28,36] The ligands of complexes **1**–**5** were prepared in one step by refluxing 2,4-pentadione with two equivalents of the corresponding aniline. The introduction of substituents at the *N*-aryl ring leads to altered catalytic properties of the β-diketiminate zinc complexes.

As a result of the successful application of β-diketimine ligands, we decided to develop a novel type of a β-diketimine ligand **10** starting from malononitrile (Scheme 1). To the best of our knowledge, so far this type has not been used in organometallic complexes. In principle, it should also be possible to synthesize chiral versions. Appropriate imine oxazoline ligands generated from chiral 1,2-amino alcohols, their corresponding zinc complexes, and their application in catalyzed copolymerization reactions of CO_2 and epoxides are known.[37]

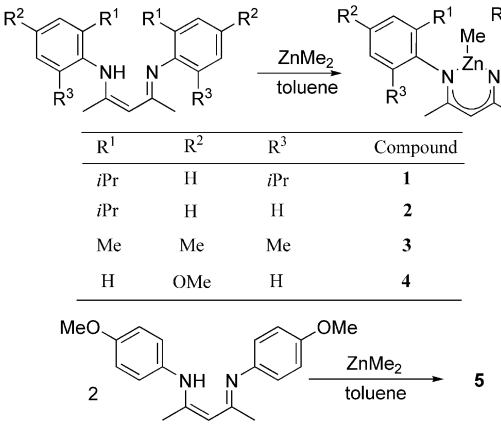


Scheme 1. Synthesis of the ligand **10**. Reagents and conditions: (a) $(CH_3)_3SiCl$, ethanol, diethylether, room temperautre, 1 h; (b) *N*-cyclohexylethane-1,2-diamine, room temperature, overnight, 37%; (c) MeLi, 0 °C, 1.5 h, 51%; (d) 2,6-diisopropylaniline, conc. HCl, ethanol, 95 °C, 4 d, 30%; (e) Amberlite® IRA-400(OH), methanol, room temperature, overnight, 81%.

For the synthesis of the ligand **10**, malononitrile was converted in one step with $(CH_3)_3SiCl$ and two equivalents of ethanol to generate in situ ethyl 2-cyano-acetimidate hydrochloride.[38] After 1 h at room temperature, *N*-cyclohexylethane-1,2-diamine[39] was added, and nitrile **8** was isolated in 37% yield. Subsequent conversion of **8** with methyllithium delivered the ketone **9** in a moderate yield of 51%. The ketone **9** was then condensed with 2,6-diisopropylaniline by heating in ethanol in the presence of HCl for 4 d at 95 °C. Ligand **10** was obtained as the hydrochloride salt by simple filtration in 30% yield. Afterwards, the free ligand **10** was easily obtained by removing the hydrochloride using Amberlite® IRA-(400)(OH) with a high yield of 81%.

Metal Complex Synthesis

The methylzinc complex **1** has been described and was prepared by reaction of dimethylzinc with the *N,N′*-bis(2,6-diisopropylphenyl)-β-diketimine.[40] The same method was used for the synthesis of compounds **2**–**5**. Complex **4** was available as a mixture with **5** (9:1), but could be obtained in pure form by crystallization. To investigate the catalytic activity of side product **5**, we used half an equivalent instead of one equivalent of dimethylzinc to yield **5** exclusively (Scheme 2).

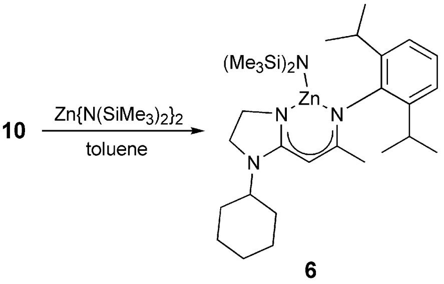


R^1	R^2	R^3	Compound
*i*Pr	H	*i*Pr	**1**
*i*Pr	H	H	**2**
Me	Me	Me	**3**
H	OMe	H	**4**

Scheme 2.

These observations are consistent with our earlier observations with ether-functionalized aminotroponimines, which give the corresponding bis(aminotroponiminate) zinc compounds.[17b]

For the preparation of the first hybrid imine imidazoline complex **6**, ligand **10** was treated with bis(trimethylsilyl)amide zinc at room temperature and **6** was isolated in a yield of 73% (Scheme 3).



Scheme 3.

All complexes have been characterized by standard analytical/spectroscopic techniques, and the molecular structures were confirmed by single-crystal X-ray diffraction in the solid state. A comparison of the ^{1}H and ^{13}C{^{1}H} NMR spectra of the starting material ZnMe$_2$ (^{1}H δ = 0.51 ppm, ^{13}C{^{1}H} δ = –4.2 ppm)[41] with the methyl complexes **2** (^{1}H δ = –0.58 ppm, ^{13}C{^{1}H} δ = –17.9 ppm), **3** (^{1}H δ = –0.56 ppm, ^{13}C{^{1}H} δ = –18.7 ppm), and **4** (^{1}H δ = –0.40 ppm, ^{13}C{^{1}H} δ = –20.8 ppm) shows that the ^{1}H NMR and the ^{13}C{^{1}H} NMR signal of the Zn–CH$_3$ group shifts to a higher field for all complexes. The observed NMR signals of the β-diketimine zinc complexes are as expected. In the NMR spectra of compound **2**, two isomers are observed. We interpret the two sets of signals in terms of hindered rotation of the 2-*i*PrC$_6$H$_4$ group around the C–N axis.

Single crystals of all the new compounds could be obtained and the solid-state structures were established by single-crystal X-ray diffraction. Only the data collected from **2** were poor and prohibited a full refinement. However, the connectivity of **2** and its composition were deduced. Compound **3** crystallizes in the monoclinic space group $P2_1/n$ and has two molecules in the asymmetric unit. As observed earlier for compound **1**, the zinc atom in compound **3** is coordinated by two nitrogen atoms and one carbon atom, which results in a planar, triangular arrangement (Figure 2). Both Zn–N bond lengths are equal within error [e.g. Zn1–N1 1.963(3) Å and Zn1–N2 1.954(3) Å]. The metallacyclohexane ring formed by the β-diketiminate ligand and the zinc atom is almost planar, which indicates a delocalization of the π electrons. The Zn–C bond length is in the expected range, Zn1–C6 1.943(4) Å and Zn2–C30 1.940(4) Å. The structure consists of individual molecules, and there are no intermolecular contacts. This is in contrast to the solid-state structure of compound **4** (Figure 3). Compound **4**, which crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell, forms a polymer in the solid state (Figure 3 bottom). The polymer is formed by intermolecular coordination of one OMe group to a zinc atom of an adjacent molecule. The Zn–O1′ bond distance is 2.368(2) Å. In contrast to compounds **2** and **3**, the Zn atom is thus four coordinate. The O1′ atom is attached almost perpendicularly to the N1–Zn–N2 plane, and the N1–Zn–O1′ and N2–Zn–O1′ bond angles are 97.31(6) and 96.00(7)°, respectively. The methyl group is slightly bent out of plane, which results in a C20–Zn–O1′ angle of 99.43(9)°. The Zn–N and Zn–C bond distances are not altered relative to compound **3** [Zn–N1 1.978(2) Å, Zn–N2 1.980(2) Å, and Zn–C20 1.962(2) Å]. The bis(β-diketiminate) complex **5** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell (Figure 4). The zinc atom is four coordinate with two ligands and forms a distorted tetrahedral environment. The N–Zn–N angles inside the metallacyclohexane ring formed by the β-diketiminato ligand and the zinc atom are N1–Zn–N2 97.78(7) and 97.42(8)°. The other N–Zn–N angles vary from 112.75(8) to 118.40(8)°.

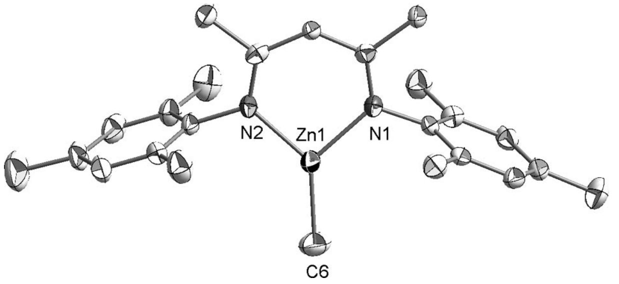


Figure 2. Perspective ORTEP view of the molecular structure of **3**. Shown is one of two crystallographic independent molecules. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–N1 1.963(3), Zn1–N2 1.954(3), Zn1–C6 1.943(4), Zn2–N3 1.967(3), Zn2–N4 1.940(3), Zn2–C30 1.940(4); N1–Zn1–C6 128.6(2), N1–Zn1–N2 96.09(13), N2–Zn1–C6 135.2(2), N4–Zn2–C30 134.8(2), N3–Zn2–N4 96.49(14), N3–Zn2–C30 128.7(2).

The Zn–N bond distances are in the expected range of 1.975(2) Å and 2.001(2) Å. Compound **6** crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell (Figure 5). The zinc atom is surrounded by three nitrogen atoms, which results in a planar triangular arrangement The Zn–N bonding distances of the asymmetric β-diketiminato ligand are in a similar range [Zn–N1 1.944(2) Å and Zn–N2 1.938(2) Å]. In contrast, the Zn–N bond of the bis(trimethylsilylamido) group is significantly shorter [Zn–N4 1.897(2) Å], which is a result of the stronger electrostatic interaction.

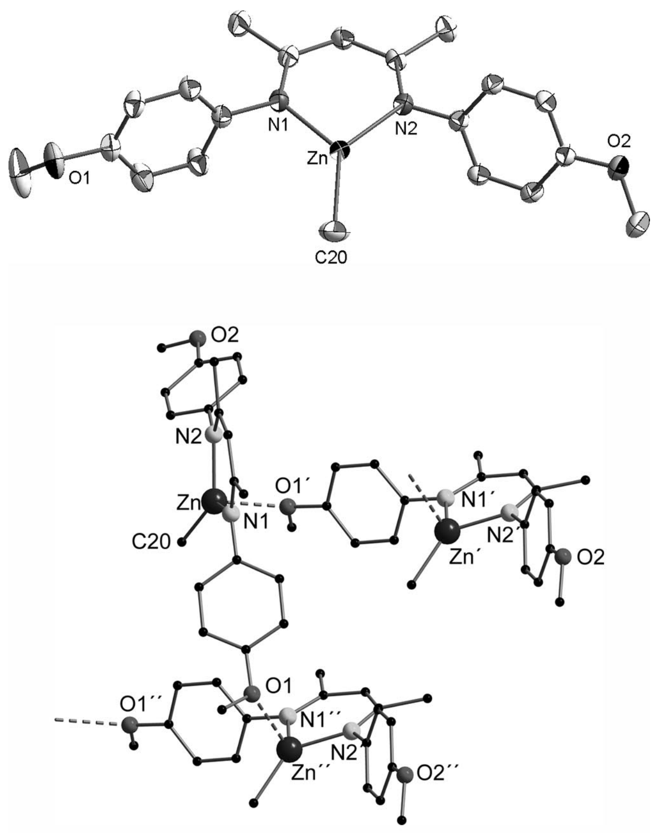


Figure 3. Perspective ORTEP view of the molecular structure of **4**. Top: thermal ellipsoids are drawn to encompass 50% probability. Bottom: perspective cut out of the polymeric solid-state structure of **4** showing the atom labelling scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn–N1 1.978(2), Zn–N2 1.980(2), Zn–C20 1.962(2), Zn–O1′ 2.368(2); N1–Zn–N2 96.07(7), N1–Zn–C20 127.17(10), N2–Zn–C20 131.04(9), N1–Zn–O1′ 97.31(6), N2–Zn–O1′ 96.00(7), C20–Zn–O1′ 99.43(9).

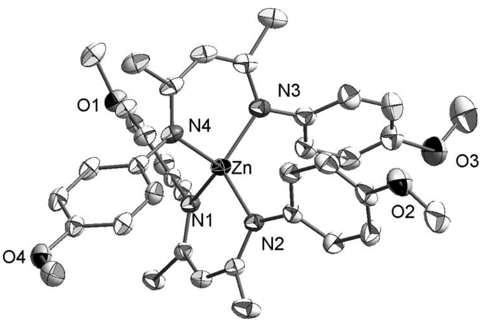


Figure 4. Perspective ORTEP view of the molecular structure of **5**. One of two crystallographic independent molecules is shown. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn–N1 1.990(2), Zn–N2 1.977(2), Zn–N3 1.975(2), Zn–N4 2.001(2); N1–Zn–N2 97.78(7), N1–Zn–N3 118.40(8), N1–Zn–N4 113.21(8), N2–Zn–N3 118.21(8), N2–Zn–N4 112.75(8), N3–Zn–N4 97.42(8).

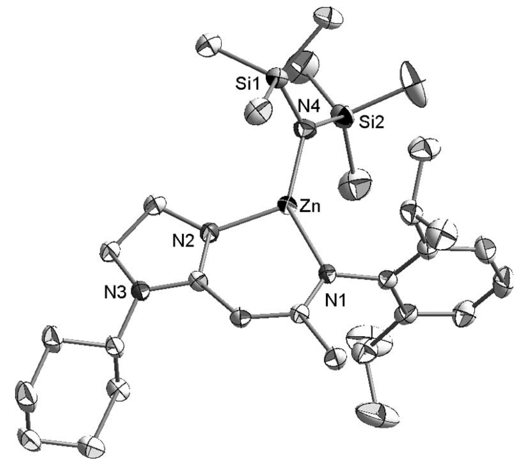
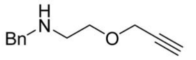
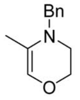
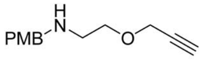
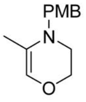
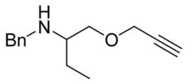
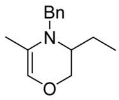
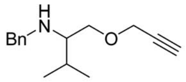
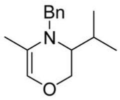
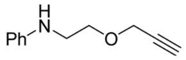
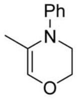
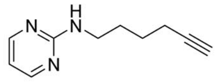
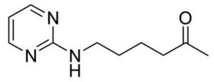
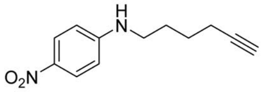
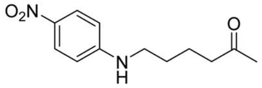


Figure 5. Perspective ORTEP view of the molecular structure of **6**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn–N1 1.944(2), Zn–N2 1.938(2), Zn–N4 1.897(2), N4–Si1 1.708(2), N4–Si2 1.708(2); N1–Zn–N2 97.52(7), N1–Zn–N4 138.65(8), N2–Zn–N4 123.48(8).

Hydroamination/Cyclization Catalysis

Encouraged by the results achieved with the hydroamination with the aminotroponiminate methyl complexes,[15–17] we applied complexes **1**–**6** as precatalysts in the intramolecular hydroamination of nonactivated alkynes (Table 1). Complexes **1**–**6** show high catalytic activity in the presence of the cocatalyst [PhNMe$_2$H][SO$_3$CF$_3$] prepared in our group. To compare the catalytic activity of complexes **1**–**6**, initial experiments were focused on the intramolecular hydroamination of the challenging substrates **11a**–**g**. The first catalyst screening experiments were carried out with substrates **11a**–**d**, and it was shown that amines with bulky substituents in the position *α* to the amine displays a significantly decreased reaction rate (Table 1, Entries 3, 4). In all cases, the generation of the cyclic products **12a**–**d** was monitored by ^{1}H NMR spectroscopy. In the cyclization reaction of the α-unsubstituted substrate **11a**, the highest catalytic activity is observed with precatalyst **1**, which required 20 h to reach a 93% conversion (Table 1, Entry 1). The more polar *p*-methoxybenzyl-protected substrate **11b** shows an even higher reaction rate (>99% within 23 h) with precatalyst **2** (Table 1, Entry 2). In comparison to **11a**, the α-ethylated substrate **11c** was converted with precatalysts **1** and **6** after longer reaction times (Table 1, Entry 3). The cyclization reaction of the α-isopropylated substrate **11d** with precatalyst **2** took only 90 h for a conversion of 98% (Table 1, Entry 4).

Table 1. Hydroamination of the aminoalkynes **11a**–**g** catalyzed by the precatalysts **1**–**6**.[a]

Entry	Substrate	Precatalyst	Time [h]	Conv. [%]	Product
1	 **11a**	**1**	**20**	**93**	 **12a**
		2	20	83	
		3	40	83	
		4	90	87	
		5	90	84	
		6	40	84	
2	 **11b**	**1**	30	96	 **12b**
		2	**23**	**>99**	
		3	40	95	
		4	70	95	
		5	40	96	
		6	40	94	
3	 **11c**	**1**	**40**	**93**	 **12c**
		2	90	98	
		3	90	97	
		4	120	74	
		5	120	73	
		6	**40**	**93**	
4	 **11d**	**1**	90	93	 **12d**
		2	**90**	**98**	
		3	100	84	
		4	100	93	
		5	100	91	
		6	90	93	
5	 **11e**	**1**	**1**	**>99**	 **12e**
		2	2	>99	
		5	2	>99	
6	 **11f**	**1**	**50**	**94/76**[b]	 **12f**
		2	140	91/59[b]	
		3	130	90	
		4	280	27	
		5	280	19	
		6	280	12	
7	 **11g**	**1**	**1**	**>99/92**[b,c]	 **12g**
		2	2	>99/89[b,c]	
		5	20	99[c]	

[a] Reagents and Conditions: Substrates **11a**–**d** (0.74 mmol), precatalyst (1 mol-%), $[PhNMe_2H][SO_3CF_3]$ (1 mol-%). Substrates **11e**–**g** (0.36 mmol), precatalyst (10 mol-%), $[PhNMe_2H][SO_3CF_3]$ (10 mol-%), C_6D_6, 60 °C. Conversions are determined by ^1H NMR spectroscopy. [b] Isolated yield after hydrolysis. [c] The reaction was performed at room temperature.

To obtain more polar substrates for the hydroamination, electronically modified *N*-aryl substrates **11e**–**g** were prepared (Table 1, Entries 5–7). At first, the substrate **11e** was introduced in cyclization reactions, and the product **12e** was observed by ^{1}H NMR spectroscopy after 1 h with precatalyst **1** in excellent conversion rates (Table 1, Entry 5). In the hydroamination of **11f**, precatalyst **1** showed the highest catalytic activity, and the ketone **12f** was isolated as product after hydrolysis of the reaction mixture in a moderate yield of 76 % (Table 1, Entry 6). In comparison to substrate **11e**, substrate **11f** showed clearly lower reaction rates, which we assign to the presence of the pyrimidyl nitrogen atoms; they decrease the catalytic activity of the zinc complexes through coordination. To prove this assumption, we introduced substrate **11g** with a less nucleophilic amine group in the hydroamination reactions and observed high conversion rates and high yields of the ketone **12g** even at room temperature. The best results were obtained with precatalyst **1**. According to these results, zinc complexes with sterically less-demanding ligands show lower catalytic activity than we have observed, particularly in the case of the zinc complexes **4** and **5** (Table 1, Entries 1–7).

Mechanistic Insight

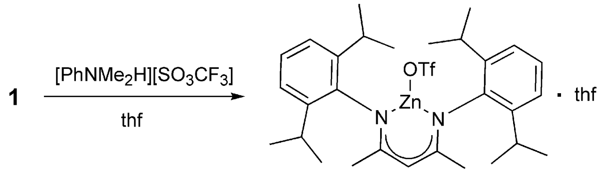
Since it is known that protons may catalyze the hydroamination reaction,[42] we treated substrate **11a** with a catalytic amount of the cocatalyst [$PhNMe_2H$][SO_3CF_3] in the absence of any zinc compound at 120 °C (Table 2, Entry 1). No reaction was observed under these conditions. In contrast, a tremendous acceleration of the reaction was measured with complex **1** as precatalyst upon addition of the cocatalyst [$PhNMe_2H$][SO_3CF_3] for all reactions shown in Table 1. Substrate **11d** is converted in 90 h at 60 °C with a precatalyst and cocatalyst loading of 1 mol-%. In comparison, **1** (catalyst loading: 10 mol-%) needs 20 d at 120 °C to reach 70 % conversion in the absence of the cocatalyst (Table 2, Entry 2). It was speculated that the cocatalyst removes the methyl group from the zinc complex in a protonation step. To prove this assumption, an equimolar mixture of precatalyst **1** and the cocatalyst [$PhNMe_2H$][SO_3CF_3] were treated to give [{*N*,*N'*-bis(2,6-diisopropylphenyl)-β-diketiminato}(trifluoromethanesulfonate)zinc]·thf (**7**) with a yield of 47 % (Scheme 4).

Table 2. Hydroamination of the aminoalkynes under various conditions.

Entry	Catalyst	Catalyst loading [%]	Cocatalyst loading [%]	*T* [°C]	Substrate	Time [h]	Conv. [h]
1	–	–	10	120	**11a**	90	0
2	**1**	10	–	120	**11d**	480	73
	1	1	1	60	**11d**	90	93
3	**1**	1	1	60	**11b**	30	96[a]
	7	1	–	60	**11b**	30	93[a]
4	**1**	1	1	60	**11c**	40	93
	$Zn(OTf)_2$	1	–	60	**11c**	120	78

[a] Yield is referred to the introduced reference compound hexamethylbenzene.

Complex **7** was characterized by standard analytical techniques, and the molecular structures were confirmed by single-crystal X-ray diffraction in the solid state. Compound **7** crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell (Figure 6). In contrast to compounds **1**–**6**, an additional equivalent of thf is coordinated to the zinc atom in the solid state, which results in a four-coordinate zinc atom. The zinc atom is thus in the center of a distorted tetrahedral coordination polyhedron.



7

Scheme 4.

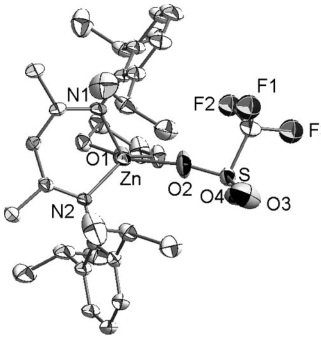


Figure 6. Perspective ORTEP view of the molecular structure of **7**. Thermal ellipsoids are drawn to encompass 50 % probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn–N1 1.854(2), Zn–N2 1.936(2), Zn–O1 2.133(2), Zn–O2 1.950(3); N1–Zn–N2 100.05(10), N1–Zn–O1 103.36(9), N1–Zn–O2 116.36(11), N2–Zn–O1 112.37(9), N2–Zn–O2 119.82(13), O1–Zn–O2 104.02(12).

Compound **7** was also tested as a catalyst in hydroamination reactions. Compound **7** converts substrate **11b** in 93 % yield with a catalyst loading of 1 mol-% and shows the same catalytic activity as the corresponding zinc catalyst generated in situ (Table 2, Entry 3).

In the hydroamination of alkynes, $Zn(OTf)_2$ was also used as a catalyst.[43] To exclude the assumption that $Zn(OTf)_2$ is generated in the reaction mixture by twofold protonation of the zinc complexes and in order to catalyze the hydroamination reaction, we tested $Zn(OTf)_2$ (catalyst loading: 1 mol-%) as catalyst to convert substrate **11c** under the same conditions described above. Interestingly, $Zn(OTf)_2$ only shows very low catalytic activity for hydroamination, whereas a 78 % conversion is observed for substrate **11c** in 5 d (Table 2, Entry 4). In the case of complex **1** (precatalyst loading: 1 mol-%) with a cocatalyst loading of 1.0 mol-%, the reaction results in 93 % conversion in 40 h (Table 1, Entry 3).

Conclusions

This work demonstrates that all the investigated complexes **1**–**6** are effective catalysts in hydroamination of nonactivated alkynes with the addition of cocatalyst

[$PhNMe_2H$][SO_3CF_3]. Subtle modifications of the ligands show dramatic effects on the catalytic activity of the complexes **1**–**6**. Thus, we suggest that accessibility to the reactive metal center is an important factor in β-diketiminate zinc complex design. However, the catalytic activities of the β-diketiminate zinc complexes **1**–**6** strongly depend on the ligand architecture and on the properties of the employed substrates. Especially, zinc complex **1** showed the highest catalytic activity in most of the cyclization reactions. It is proposed that the high steric bulk of precatalyst **1** protects the Lewis acid zinc center from high polar functional groups but allows interactions for the cyclization process. In this context, it was possible to isolate the intermediate, which was formed by reaction of precatalyst **1** and cocatalyst [$PhNMe_2H$][SO_3CF_3]. The resulting zinc catalyst **7** showed the same catalytic activity in hydroamination reactions as did the precatalyst **1**. The novel imidazoline zinc complex **6** also showed high catalytic activity in hydroamination reactions. But unlike the β-diketimine complexes **1**–**5**, the advantage of the imidazoline zinc complex system is that the synthetic route to this new type of ligands allows the introduction of chiral centers such as chiral 1,2-diamines for catalyzed asymmetric synthesis. Further studies are under current investigations.

Experimental Section

General Methods and Instruments: All reactions with air- or water-sensitive compounds were carried out under dry nitrogen with standard Schlenk vacuum-line techniques. All NMR-tube scale reactions were prepared in an N_2-filled glove box. NMR spectra were recorded on a Bruker AC 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) and DRX 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) spectrometer and referenced versus residual solvent shifts. The ratio between the substrate and the product was calculated exactly by comparison of the integration of the corresponding signals. All products were analyzed by ^{1}H, ^{13}C, ^{13}C-DEPT, COSY, and HMQC NMR spectroscopy and by IR spectroscopy, MS, HRMS and EA where possible. Infrared spectra were recorded on a Perkin–Elmer spectrometer 881 as ATR (Attenuated Total Reflectance). MS and HRMS analyses were carried out with a Finnigan MAT 95 SQ or a Varian MAT 711 spectrometer. Elemental analyses were carried out with a Vario EL III instrument. Melting points were determined in sealed glass capillaries under N_2 with BÜCHI 535. The substrates **11b**–**d** and their cyclic hydroamination products **12b**–**d** were previously described in our group.[15] Prior to use, all substrates were purified by bulb-to-bulb distillation or by flash column chromatography over silica gel (40-63 µm). Toluene, thf, and diethyl ether were distilled under nitrogen from sodium, hexane was distilled under nitrogen from calcium hydride, and C_6D_6 was stored over K/Na alloy before use. Dimethylzinc and the starting materials for the preparation of the substrates **11a**–**g** were purchased from Acros Organics, Aldrich and Fluka.

Hydroamination: The aminoalkynes (740 µmol) were dissolved in C_6D_6 (0.5 mL) and added to the precatalyst (e.g. 7.40 µmol for 1 mol-%) and then to the cocatalyst [$PhNMe_2H$][SO_3CF_3] (7.40 µmol for 1 mol-%). The mixture was injected into an NMR tube, removed from the glovebox, cooled to –196 °C, and flame-sealed under vacuum. The reaction mixture was then heated to 60 °C for the stated duration of time. The hydroamination products were purified by flash column chromatography on silica gel.

Ligand Synthesis

(1-Cyclohexyl-imidazolidine-2-ylidene)acetonitrile (8): To a solution of malononitrile (255 mg, 3.86 mmol) and ethanol (415 mg, 9.01 mmol) in diethyl ether (4 mL) was added $(CH_3)_3SiCl$ (424 mg, 3.90 mmol). After 1 h at room temperature *N*-cyclohexylethane-1,2-diamine (538 mg, 3.78 mmol) was added, and the suspension was stirred overnight. After the addition of concentrated $NaHCO_3$ solution, the mixture was extracted with diethyl ether (2 × 100 mL) and dried with $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2, cyclohexane/EtOAc, 1:3) to afford **8** as a white solid. Yield: 271 mg (37%). M.p. 164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.12 (m, 1 H, CH_2), 1.33 (m, 4 H, CH_2), 1.70 (m, 1 H, CH_2), 1.85 (m, 4 H, CH_2), 3.05 (s, 1 H, CH), 3.09 (m, 1 H, CH), 3.45 (m, 4 H, CH_2), 4.67 (br. s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.4 (CH_2), 25.5 (CH_2), 29.6 (CH_2), 35.4 (CH), 41.9 (CH_2), 44.0 (CH_2), 53.9 (CH), 124.2 (C), 163.8 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3299, 2934, 2856, 2168, 1586, 1503, 1279, 1076, 968 cm^{-1}. MS (EI, 70 eV, room temperature): *m*/*z* (%) = 191 (42) [M^+], 148 (40), 109 (100), 80 (61), 69 (25), 55 (35), 45 (48), 41 (69). HRMS: calcd. for $C_{11}H_{17}N_3$ 191.1423; found 191.1415.

1-(1-Cyclohexyl-imidazolidine-2-ylidene)propan-2-one (9): Compound **8** (778 mg, 4.06 mmol) in thf (9 mL) was added dropwise to a solution of methyllithium (1.6 M in diethylether, 13 mL, 20.80 mmol) at –10 °C, and the solution was stirred for 1.5 h at 0 °C. After the addition of HCl [1 M] at –30 °C, the mixture was extracted with diethyl ether (2 × 60 mL) and dried with $MgSO_4$. The solvent was concentrated under reduced pressure, and the residue was recrystallized at –20 °C to obtain **9** as white crystals. Yield: 435 mg (51%). M.p. 120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.11 (m, 1 H, CH_2), 1.35 (m, 4 H, CH_2), 1.70 (m, 1 H, CH_2), 1.81 (m, 4 H, CH_2), 2.00 (s, 3 H, CH_3), 3.31 (m, 1 H, CH), 3.39 (m, 2 H, CH_2), 3.55 (m, 2 H, CH_2), 4.61 (s, 1 H, CH), 9.37 (br. s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.5 (CH_2), 25.6 (CH_2), 28.8 (CH_3), 30.0 (CH_2), 42.0 (CH_2), 42.6 (CH_2), 53.2 (CH), 75.6 (CH), 162.8 (C), 191.0 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3262, 2931, 2861, 1594, 1542, 1512, 1281, 1223, 1071, 960, 716, 676 cm^{-1}. MS (EI, 70 eV, room temperature): *m*/*z* (%) = 208 (56) [M^+], 193 (9), 153 (18), 84 (100), 43 (52). HRMS: calcd. for $C_{12}H_{20}N_2O$ 208.1576; found 208.1578.

[2-(1-Cyclohexyl-imidazolidine-2-ylidene)-1-methylethylidene]-(2,6-diisopropylphenyl)amino Hydrochloride (10·HCl): A solution of **9** (867 mg, 4.16 mmol) and 2,6-diisopropylaniline (870 mg, 4.91 mmol) in ethanol (15 mL) and concentrated HCl (0.7 mL) were heated for 4 d at 95 °C. Chloroform (7 mL) and ether (30 mL) were then added to the solvent. After 24 h at –20 °C, the suspension was filtered and **10·HCl** was obtained as a white powder. Yield: 500 mg (30%). M.p. >230 °C. ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 0.92 (m, 3 H, CH_2), 1.13 (d, *J* = 6.8 Hz, 12 H, CH_3), 1.39 (m, 5 H, CH_2), 1.63 (m, 2 H, CH_2), 2.47 (s, 3 H, CH_3), 2.82 (tt, *J* = 3.8, *J* = 11.5 Hz, 1 H, CH), 2.90 (septet, *J* = 6.8 Hz, 2 H, CH), 3.59 (br. s, 4 H, CH_2), 3.87 (s, 1 H, CH), 7.28 (m, 2 H, CH_{Ar}), 7.38 (m, 1 H, CH_{Ar}), 8.29 (br. s, 1 H, NH), 9.44 (br. s, 1 H, HCl) ppm. ^{13}C NMR (125 MHz, [D_6]DMSO): δ = 19.4 (CH_3), 23.1 (CH_3), 24.4 (CH_3), 24.5 (CH_2), 25.0 (CH_2), 28.0 (CH), 29.4 (CH_2), 41.8 (CH_2), 43.5 (CH_2), 54.4 (CH), 74.5 (CH), 123.9 (CH_{Ar}), 128.9 (CH_{Ar}), 132.6 (C), 145.9 (C), 162.4 (C), 162.8 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3156, 3103, 2961, 2933, 2863, 1700, 1596, 1574, 1531, 1452, 1383, 1280, 1041, 800 cm^{-1}. MS (EI, 70 eV, 160 °C): *m*/*z* (%) = 367

(47) [M$^+$ – HCl], 352 (26), 324 (72), 200 (59), 166 (57), 153 (82), 84 (100). HRMS: calcd. for $C_{24}H_{37}N_3$ 367.2988; found 367.2988.

[2-(1-Cyclohexyl-imidazolidine-2-ylidene)-1-methylethylidene]-(2,6-diisopropylphenyl)amine (10): To a solution of **10**·HCl (470 mg, 1.16 mmol) in methanol (10 mL) was added Amberlite® IRA-400(OH) (3 mL), and the suspension was stirred overnight. After filtration of the mixture, the filtrate was concentrated under reduced pressure. The crude product was then dissolved in ether and filtered over Celite®. After concentration of the filtrate, **10** was obtained as a colorless oil that crystallized to a white solid overnight. Yield: 346 mg (81%). M.p. 116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.13 (d, J = 6.8 Hz, 6 H, CH_3), 1.17 (d, J = 7.0 Hz, 6 H, CH_3), 1.38 (m, 4 H, CH_2), 1.63 (s, 3 H, CH_3), 1.70 (m, 2 H, CH_2), 1.84 (m, 4 H, CH_2), 3.10 (septet, J = 6.9 Hz, 2 H, CH), 3.26 (t, J = 8.8 Hz, 2 H, CH_2), 3.55 (m, 1 H, CH), 3.63 (t, J = 8.8 Hz, 2 H, CH_2), 4.42 (s, 1 H, CH), 7.11 (m, 3 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.8 (CH_3), 22.9 (CH_3), 24.5 (CH_3), 25.8 (CH_2), 25.9 (CH_2), 28.1 (CH), 30.3 (CH_2), 43.3 (CH_2), 48.4 (CH_2), 53.7 (CH), 77.2 (CH), 122.9 (CH_{Ar}), 125.2 (CH_{Ar}), 128.9 (C), 144.3 (C), 163.1 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3061, 2959, 2931, 2856, 1626, 1528, 1451, 1387, 1312, 1276, 1172, 759 cm^{-1}. MS (EI, 70 eV, 230 °C): *m*/*z* (%) = 368 (71) [M$^+$ + H], 353 (49), 324 (100), 242 (28), 202 (68), 200 (71), 153 (80), 84 (97). HRMS: calcd. for $C_{24}H_{38}N_3$ 208.1576; found 208.1578. $C_{24}H_{37}N_3$ (367.58): calcd. C 78.42, H 10.15, N 11.43; found C 78.06, H 10.46, N 11.30.

Metal-Complex Synthesis

[{*N,N′*-Bis(2-isopropylphenyl)-β-diketiminato}methylzinc] (2): To a solution of $ZnMe_2$ (1.2 M in toluene, 2.5 mL, 3 mmol) in toluene (5 mL) was slowly added a solution of the corresponding ligand (200 mg, 0.6 mmol) in toluene (5 mL) at –20 °C. The reaction mixture was warmed up to room temperature and stirred overnight at 80 °C. The clear solution was concentrated in vacuo and dried at 60 °C to give a quantitative yield of the desired compound as a yellowish oil, which crystallized in 3 d to a white solid. M.p. 105 °C. ^{1}H NMR [400 MHz, C_6D_6, mixture of *E*/*E* and *E*/*Z* isomers (1:1)]: δ = –0.58 (s, 3 H, CH_3), –0.53 (s, 3 H, CH_3), 1.13 (d, J = 6.9 Hz, 6 H, CH_3), 1.16 (d, J = 6.9 Hz, 6 H, CH_3), 1.20 (d, J = 6.9 Hz, 6 H, CH_3), 1.25 (d, J = 6.9 Hz, 6 H, CH_3), 1.76 (s, 6 H, CH_3), 1.78 (s, 6 H, CH_3), 3.27 (m, 4 H, CH), 4.96 (s, 1 H, CH), 5.02 (s, 1 H, CH), 6.83 (m, 4 H, CH_{Ar}), 7.05 (m, 8 H, CH_{Ar}), 7.22 (m, 4 H, CH_{Ar}) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = –17.9 (CH_3), –17.9 (CH_3), 22.8 (CH_3), 23.1 (CH_3), 23.2 (CH_3), 23.3 (CH_3), 23.5 (CH_3), 23.6 (CH_3), 27.8 (CH), 27.8 (CH), 95.7 (CH), 95.9 (CH), 124.8 (CH_{Ar}), 125.0 (CH_{Ar}), 125.3 (CH_{Ar}), 125.4 (CH_{Ar}), 125.9 (CH_{Ar}), 126.0 (CH_{Ar}), 126.3 (CH_{Ar}), 126.3 (CH_{Ar}), 141.5 (C), 141.6 (C), 147.3 (C), 147.4 (C), 166.6 (C), 166.8 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3623, 3063, 3019, 2960, 2926, 2867, 1646, 1626, 1596, 1554, 1520, 1480, 1443, 1407, 1365, 1341, 1282, 1209, 1183, 1086, 1032, 941, 838, 753, 658 cm^{-1}. MS (EI, 70 eV, 120 °C): *m*/*z* (%) = 412 (57) [M$^+$], 397 (100) [M$^+$ – Me], 333 (22), 200 (10), 160 (58), 158 (28), 144 (24). HRMS: calcd. for $C_{24}H_{32}N_2Zn$ 412.1857; found 412.1855. $C_{24}H_{32}N_2Zn$ (413.91): calcd. C 69.64, H 7.55, N 6.77; found C 69.30, H 7.64, N 6.33.

[{*N,N′*-Bis(2,4,6-trimethylphenyl)-β-diketiminato}methylzinc] (3): The synthesis was similar to that of **2**. Compound **3** was isolated in quantitative yield as a white powder. M.p. 117 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = –0.56 (s, 3 H, CH_3), 1.68 (s, 6 H, CH_3), 2.17 (s, 12 H, CH_3), 2.19 (s, 6 H, CH_3), 5.03 (s, 1 H, CH), 6.86 (s, 4 H, CH_{Ar}) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = –18.7 (CH_3), 18.4 (CH_3), 20.6 (CH_3), 22.3 (CH_3), 95.4 (CH), 129.2 (CH_{Ar}), 130.5 (C), 133.4 (C), 145.2 (C), 166.8 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3687, 2999, 2911, 2852, 1663, 1546, 1524, 1456, 1401, 1375, 1261, 1233, 1205, 1149, 1101, 1016, 857, 836, 746, 730, 657 cm^{-1}. MS (EI, 70 eV, 170 °C): *m*/*z* (%) = 412 (75) [M$^+$], 397 (100) [M$^+$ – Me], 333 (25), 279 (17), 172 (13), 160 (63), 158 (18), 145 (14), 119 (35), 91 (17). HRMS: calcd. for $C_{24}H_{32}N_2Zn$ 412.1857; found 412.1852. $C_{24}H_{32}N_2Zn$ (413.91): calcd. C 69.64, H 7.79, N 6.77; found C 69.58, H 7.97, N 6.65.

[{*N,N′*-Bis(4-methoxyphenyl)-β-diketiminato}methylzinc] (4): A solution of $ZnMe_2$ (1.2 M in toluene, 4 mL, 4.8 mmol) in toluene (10 mL) was treated dropwise with a solution of the corresponding ligand (300 mg, 0.97 mmol) in toluene (10 mL) at –20 °C over 3 h. The reaction mixture was slowly warmed up to room temperature and stirred overnight. The yellow solution was concentrated in vacuo and dried at 60 °C to give 90% of the desired compound **4** and 10% by-product **5** as a brown solid. ^{1}H NMR (400 MHz, C_6D_6): δ = –0.40 (s, 3 H, CH_3), 1.91 (s, 6 H, CH_3), 3.33 (s, 6 H, OCH_3), 4.97 (s, 1 H, CH), 6.77 (m, 8 H, CH_{Ar}) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = –20.8 (CH_3), 23.1 (CH_3), 54.6 (CH_3), 96.9 (CH), 114.1 (CH_{Ar}), 125.4 (CH_{Ar}), 143.0 (C), 156.7 (C), 166.3 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3633, 3033, 2954, 2832, 1606, 1550, 1500, 1455, 1401, 1271, 1238, 1199, 1179, 1103, 1033, 939, 861, 822, 654 cm^{-1}. MS (EI, 70 eV, 100 °C): *m*/*z* (%) = 388 (81) [M$^+$], 373 (100) [M$^+$ – Me], 358 (38), 328 (9), 309 (35), 267 (27), 189 (8), 148 (52), 146 (11), 92 (11), 79 (12), 77 (16), 69 (20), 57 (8). HRMS: calcd. for $C_{20}H_{24}N_2O_2Zn$ 388.1129; found 388.1136.

[Bis{*N,N′*-bis(4-methoxyphenyl)-β-diketiminato}zinc] (5): A solution of the corresponding ligand (300 mg, 0.97 mmol) in toluene (5 mL) was treated dropwise with $ZnMe_2$ (1.2 M in toluene, 0.5 mL, 0.6 mmol) for 0.5 h at room temperature and stirred overnight. The yellow solution was dried in vacuo at 60 °C to give a quantitative yield of the desired compound as a yellow powder. M.p. 159 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 1.85 (s, 12 H, CH_3), 3.36 (s, 12 H, CH_3), 4.69 (s, 2 H, CH), 6.85 (m, 16 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 23.0 (CH_3), 54.6 (CH_3), 95.7 (CH), 113.8 (CH_{Ar}), 125.5 (CH_{Ar}), 143.8 (C), 156.3 (C), 166.1 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3033, 2950, 2832, 1625, 1606, 1549, 1500, 1453, 1399, 1269, 1238, 1199, 1180, 1104, 1035, 939, 860, 821, 785 cm^{-1}. MS (EI, 70 eV, 210 °C): *m*/*z* (%) = 682 (79) [M$^+$], 667 (6), 561 (22), 373 (21), 341 (9), 309 (32), 189 (45), 148 (83), 92 (100), 69 (28). HRMS: calcd. for $C_{38}H_{42}N_4O_4Zn$ 682.2498; found 682.2505. $C_{38}H_{42}N_4O_4Zn$ (684.15): calcd. C 66.71, H 6.19, N 8.19; found C 66.38, H 6.25, N 8.13.

[{2-(1-Cyclohexyl-imidazolidine-2-ylidene)-1-methylethylidene-(2,6-diisopropylphenyl)aminato}bis(trimethysilylamido)zinc] (6): A solution of $Zn\{N(SiMe_3)_2\}_2$ (246 mg, 0.64 mmol) in hexane (5 mL) was treated dropwise with **9** (216 mg, 0.59 mmol) in hexane (5 mL) and stirred overnight at room temperature. Subsequently, the solution was concentrated at reduced pressure, and the crude product was recrystallized at –20 °C. Compound **6** was obtained as white crystals. Yield: 255 mg (73%). M.p. 164 °C. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.29 (s, 18 H, CH_3), 0.88 (m, 1 H, CH_2), 1.07 (m, 4 H, CH_2), 1.22 (d, J = 6.8 Hz, 6 H, CH_3), 1.41 (d, J = 6.9 Hz, 6 H, CH_3), 1.45 (m, 1 H, CH_2), 1.60 (m, 4 H, CH_2), 1.76 (s, 3 H, CH_3), 2.86 (t, J = 9.2 Hz, 2 H, CH_2), 3.31 (m, 1 H, CH), 3.42 (septet, J = 6.8 Hz, 2 H, CH), 3.75 (t, J = 9.2 Hz, 2 H, CH_2), 4.60 (s, 1 H, CH), 7.20 (m, 3 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 5.4 (CH_3), 24.5 (CH_3), 24.8 (CH_3), 24.9 (CH_3), 25.7 (CH_2), 25.9 (CH_2), 28.2 (CH), 30.3 (CH_2), 43.2 (CH_2), 48.9 (CH_2), 53.7 (CH), 77.0 (CH), 124.0 (CH_{Ar}), 125.8 (CH_{Ar}), 143.1 (C), 145.5 (C), 165.2 (C), 166.8 (C) ppm. MS (EI, 70 eV, 90 °C): *m*/*z* (%) = 590 (5) [M$^+$], 575 (10), 429 (50), 202 (14), 146 (100), 130 (56), 73 (9). HRMS: calcd. for $C_{30}H_{53}N_4Si_2Zn$ 589.3100; found 589.3090. $C_{30}H_{54}N_4Si_2Zn$ (592.34): calcd. C 60.83, H 9.19, N 9.46; found C 60.16, H 9.65, N 9.25.

[{*N*,*N*′-Bis(2,6-diisopropylphenyl)-β-diketiminato}(trifluoromethanesulfonato)zinc]·thf (7): To a solution of **1** (200 mg, 0.40 mmol) in thf (3 mL) was added the cocatalyst $[PhNMe_2H][SO_3CF_3]$ (109 mg, 0.40 mmol). The reaction mixture was stirred overnight at 60 °C in a sealed tube. The clear solution was heated for 2 h at 120 °C and recrystallized at room temperature to give **7** as white crystals. Yield: 132 mg (47%). ^{1}H NMR (400 MHz, C_6D_6): δ = 1.20 (d, *J* = 6.8 Hz, 12 H, CH_3), 1.26 (m, 4 H, CH_2), 1.39 (d, *J* = 6.6 Hz, 12 H, CH_3), 1.63 (s, 6 H, CH_3), 3.29 (m, 4 H, CH), 3.55 (m, 4 H, CH_2), 4.77 (s, 1 H, CH), 7.18 (m, 6 H, CH_{Ar}) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 23.9 (CH_3), 24.4 (CH_3), 24.5 (CH_3), 25.2 (CH_2), 28.3 (CH), 70.6 (CH_2), 95.3 (CH), 124.3 (CH_{Ar}), 126.7 (CH_{Ar}), 142.9 (C), 143.4 (C), 170.6 (C) ppm. ^{19}F NMR (470.6 MHz, $CDCl_3$): δ = –77.42 ppm. IR (ATR): $\tilde{\nu}$ = 3473, 3222, 3055, 2964, 2931, 2870, 1700, 1549, 1462, 1277, 1240, 1165, 1030, 800, 758 cm^{-1}.

Catalysis

***N*,*N*′-Dimethylphenylammonium Trifluoromethanesulfonate $[PhNMe_2H][SO_3CF_3]$:** To a solution of *N*,*N*′-dimethylphenylamine (1.5 g, 12.5 mmol) in hexane (20 mL) was added trifluoromethane sulfonic acid (1.9 g, 12.5 mmol); the mixture was stirred for 1 h at room temperature. Subsequently, the solution was concentrated at reduced pressure and $[PhNMe_2H][SO_3CF_3]$ was obtained quantitatively as a colorless oil that crystallized to colorless crystals upon standing. M.p. 38 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.31 (d, *J* = 5.0 Hz, 6 H, CH_3), 7.54 (m, 5 H, CH_{Ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 47.4 (CH_3), 120.2 (CH_{Ar}), 120.4 (CF_3), 130.8 (CH_{Ar}), 130.9 (CH_{Ar}), 142.1 (C) ppm. ^{19}F NMR (470.6 MHz, $CDCl_3$): δ = –78.09 ppm. IR (ATR): $\tilde{\nu}$ = 3472, 3052, 2771, 1497, 1282, 1239, 1160, 1027, 900, 767, 693 cm^{-1}. MS (EI, 70 eV, 80 °C): *m*/*z* (%) = 121 (75), 120 (100), 105 (13), 77 (22), 51 (9). $C_{19}H_{12}F_3NO_3S$ (391.36): calcd. C 39.85, H 4.46, N 5.16; found C 39.51, H 4.47, N 5.21.

***N*-Benzyl-(2-prop-2-ynyloxyethyl)amine (11a):** 2-(Benzylideneamino)ethanol (3.0 g, 20.1 mmol) in thf (20 mL) was added to a suspension of NaH (60% in mineral oil, 1.2 g, 30.0 mmol) and 3-bromopropyne (80% in toluene, 3.4 mL, 30.2 mmol) in thf (30 mL). The reaction mixture was heated for 3 h at 60 °C and then left at room temperature overnight. After the aqueous workup and extraction with diethyl ether (2 × 30 mL), the organic phase was first washed with water (40 mL) and then with a concentrated NaCl solution (40 mL). Subsequently, the crude product was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by bulb-to-bulb distillation (4.0×10^{-2} mbar, 125 °C) to afford *N*-benzylidene(2-prop-2-ynyloxyethyl)amine as a yellowish oil. Yield: 3.5 g (93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (t, *J* = 2.3 Hz, 1 H, CH), 3.84 (m, 4 H, CH_2), 4.19 (d, *J* = 2.3 Hz, 2 H, CH_2), 7.41 (m, 3 H, CH_{Ar}), 7.74 (m, 2 H, CH_{Ar}), 8.32 (s, 1 H, CH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.7 (CH_2), 62.5 (CH_2), 63.2 (CH_2), 77.2 (CH), 92.6 (C), 128.2 (CH_{Ar}), 128.6 (CH_{Ar}), 130.9 (CH_{Ar}), 135.9 (C), 163.1 (CH) ppm. IR (ATR): $\tilde{\nu}$ = 3293, 3061, 3027, 2850, 1647, 1451, 1100, 1032, 918, 755, 693 cm^{-1}. MS (EI, 70 eV, room temperature): *m*/*z* (%) = 186 (29) [M^+ – H], 156 (3), 133 (28), 118 (76), 104 (21), 91 (100), 77 (9), 65 (8), 51 (9). HRMS: calcd. for $C_{12}H_{12}NO$ 186.0919; found 186.0915.

The isolated imine intermediate (3.3 g, 17.6 mmol) was then dissolved in methanol (50 mL) and $NaBH_4$ (2.7 g, 71.3 mmol) was added at 0 °C. After 1 h at 0 °C, the reaction mixture was stirred overnight at room temperature and then concentrated at reduced pressure. After aqueous workup and extraction with diethyl ether (3 × 30 mL), the organic phase was washed with water (40 mL), then with a concentrated NaCl solution (40 mL), and dried with $MgSO_4$. After concentration of the crude product under reduced pressure and purification by bulb-to-bulb distillation (4.0×10^{-2} mbar, 150 °C), **11c** was obtained as a yellowish oil. Yield: 2.7 g (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.71 (s, 1 H, NH), 2.42 (t, *J* = 2.3 Hz, 1 H, CH), 2.84 (t, *J* = 5.1 Hz, 2 H, CH_2), 3.66 (t, *J* = 5.1 Hz, 2 H, CH_2), 3.82 (s, 2 H, CH_2), 4.15 (d, *J* = 2.3 Hz, 2 H, CH_2), 7.29 (m, 5 H, CH_{Ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 48.6 (CH_2), 53.8 (CH_2), 58.3 (CH_2), 69.4 (CH_2), 74.4 (CH), 79.7 (C), 126.9 (CH_{Ar}), 128.2 (CH_{Ar}), 128.4 (CH_{Ar}), 140.2 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3294, 3027, 2920, 2853, 1453, 1353, 1099, 737, 699 cm^{-1}. MS (EI, 70 eV, room temperature): *m*/*z* (%) = 189 (64) [M^+], 160 (4), 120 (5), 98 (20), 92 (9), 91 (100), 65 (11). HRMS: calcd. for $C_{12}H_{15}NO$ 189.1154; found 189.1151.

Phenyl(2-prop-2-ynyloxyethyl)amine (11e): To a solution of *N*-phenylaminoethanol (6.0 g, 43.7 mmol) in thf (100 mL) was added NaH (75% in mineral oil, 2.1 g, 65.6 mmol) at –20 °C. After 0.5 h, 3-bromopropyne (80% in toluene, 5.1 mL, 45.7 mmol) was added, and the reaction mixture was stirred overnight at room temperature. After aqueous workup and extraction with diethyl ether (3 × 150 mL), the crude product was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by bulb-to-bulb distillation (2.9 mbar, 175 °C) to afford **11f** as a yellowish oil. Yield: 6.9 g (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.51 (dt, *J* = 0.6, *J* = 2.4 Hz, 1 H, CH), 3.36 (dt, *J* = 2.8, *J* = 5.4 Hz, 2 H, CH_2), 3.78 (dt, *J* = 2.8, *J* = 5.6 Hz, 2 H, CH_2), 3.97 (br. s, 1 H, NH), 4.22 (dt, *J* = 0.6, *J* = 2.4 Hz, 2 H, CH_2), 6.68 (m, 2 H, CH_{Ar}), 6.77 (m, 1 H, CH_{Ar}), 7.23 (m, 2 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 43.5 (CH_2), 58.3 (CH_2), 68.5 (CH_2), 74.9 (CH), 79.7 (C), 113.2 (CH_{Ar}), 117.7 (CH_{Ar}), 126.3 (CH_{Ar}), 148.2 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3400, 3285, 2924, 2855, 1602, 1505, 1318, 1264, 1095, 749, 693 cm^{-1}. MS (EI, 70 eV, room temperature): *m*/*z* (%) = 175 (18) [M^+], 106 (100), 77 (12). HRMS: calcd. for $C_{11}H_{13}NO$ 175.0997; found 175.0996.

Hex-5-ynylpyrimidin-2-ylamine (11f): Hex-5-ynylamine (806 mg, 8.30 mmol), 2-chloropyrimidine (1.2 g, 10.5 mmol), and K_2CO_3 (1.0 g, 7.2 mmol) were stirred in dmf (20 mL) for 2 d at 70 °C. After aqueous workup and extraction with dichloromethane (2 × 100 mL), the crude product was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, cyclohexane/EtOAc, 3:1) to afford **11e** as a white solid. Yield: 963 mg (66%). M.p. 59 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.62 (m, 2 H, CH_2), 1.74 (m, 2 H, CH_2), 1.95 (t, *J* = 2.6 Hz, 1 H, CH), 2.24 (dt, *J* = 2.6, *J* = 6.9 Hz, 2 H, CH_2), 3.43 (dt, *J* = 5.9, *J* = 7.0 Hz, 2 H, CH_2), 5.24 (br. s, 1 H, NH), 6.50 (t, *J* = 4.8 Hz, 1 H, CH_{Ar}), 8.26 (d, *J* = 4.8 Hz, 2 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.2 (CH_2), 25.8 (CH_2), 28.7 (CH_2), 40.9 (CH_2), 68.6 (CH), 84.1 (C), 110.4 (CH_{Ar}), 158.0 (CH_{Ar}), 162.4 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3231, 2943, 2868, 1593, 1535, 1451, 1379, 1120, 801, 686 cm^{-1}. MS (EI, 70 eV, room temperature): *m*/*z* (%) = 174 (11) [M^+ – H], 146 (20), 136 (9), 108 (100), 95 (11), 79 (14). HRMS: calcd. for $C_{10}H_{12}N_3$ 174.1031; found 174.1031.

Hex-5-ynyl-(4-nitro-phenyl)-amine (11g): Hex-5-ynylamine (629 mg, 6.47 mmol), 1-fluoro-4-nitrobenzene (1.1 g, 7.8 mmol), and K_2CO_3 (630 mg, 4.56 mmol) were stirred in dmf (10 mL) overnight. After aqueous workup and extraction with diethyl ether (2 × 100 mL), the crude product was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, cyclohexane/ether, 3:1) to afford **11g** as yellow crystals. Yield: 1.0 g (72%). M.p. 60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.65 (m, 2 H, CH_2), 1.81 (m, 2 H, CH_2), 1.99 (t, *J* = 2.6 Hz, 1 H, CH), 2.27 (dt, *J* = 2.6, *J* = 6.9 Hz, 2 H, CH_2), 3.25 (t, *J* = 7.1 Hz, 2 H, CH_2), 4.64 (br. s, 1 H, NH), 6.53 (m, 2 H,

CH_{Ar}), 8.09 (m, 2 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.1 (CH_2), 25.7 (CH_2), 28.0 (CH_2), 43.0 (CH_2), 69.1 (CH), 83.7 (C), 111.2 (CH_{Ar}), 126.5 (CH_{Ar}), 138.1 (C), 153.1 (C) ppm. IR (ATR): ṽ = 3376, 3292, 2941, 2864, 1600, 1470, 1302, 1184, 1111, 832, 753 cm^{-1}. MS (EI, 70 eV, room temperature): *m*/*z* (%) = 218 (16) [M^+], 166 (10), 151 (100), 105 (35), 84 (19). HRMS: calcd. for $C_{12}H_{14}N_2O_2$ 218.1055; found 218.1042.

4-Benzyl-5-methyl-3,4-dihydro-2*H*-[1,4]oxazine (12a): Compound **12a** was prepared according to the method described in the General Methods and Instruments Section and was characterized after concentration of the reaction mixture under reduced pressure. ^1H NMR (400 MHz, C_6D_6): δ = 1.62 (d, *J* = 1.1 Hz, 3 H, CH_3), 2.72 (t, *J* = 4.2 Hz, 2 H, CH_2), 3.62 (t, *J* = 4.2 Hz, 2 H, CH_2), 3.70 (s, 3 H, CH_2), 5.99 (q, *J* = 1.2 Hz, 1 H, CH), 7.15 (m, 1 H, CH_{Ar}), 7.22 (m, 4 H, CH_{Ar}) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 15.9 (CH_3), 47.4 (CH_2), 55.0 (CH_2), 62.2 (CH_2), 121.4 (C), 125.3 (CH), 127.2 (CH_{Ar}), 128.4 (CH_{Ar}), 128.6 (CH_{Ar}), 139.5 (C) ppm. IR (ATR): ṽ = 3381, 3085, 3062, 3027, 2957, 2926, 2853, 1713, 1652, 1604, 1585, 1540, 1495, 1452, 1361, 1317, 1252, 1202, 1160, 1126, 1090, 1070, 1028, 999, 973, 895, 822, 731, 698 cm^{-1}. MS (EI, 70 eV, 100 °C): *m*/*z* (%) = 189 (42) [M^+], 98 (14), 92 (7), 91 (100), 70 (7), 65 (16), 63 (4), 56 (3), 51 (5). HRMS: calcd. for $C_{12}H_{15}NO$ 189.1154; found 189.1154.

5-Methyl-4-phenyl-3,4-dihydro-2*H*-[1,4]oxazine (12e): Compound **12e** was prepared according to the method described in the General Methods and Instruments Section and was characterized according to the literature[15] by NMR spectroscopy. ^1H NMR (400 MHz, C_6D_6): δ = 1.61 (t, *J* = 1.0 Hz, 3 H, CH_3), 3.19 (dt, *J* = 0.8, *J* = 4.1 Hz, 2 H, CH_2), 3.59 (dt, *J* = 0.8, *J* = 4.1 Hz, 2 H, CH_2), 6.17 (t, *J* = 1.0 Hz, 1 H, CH), 6.91 (m, 3 H, 1-H, CH_{Ar}), 7.17 (m, 2 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ = 15.9 (CH_3), 51.5 (CH_2), 62.0 (CH_2), 116.8 (C), 122.3 (CH_{Ar}), 123.4 (CH_{Ar}), 129.2 (CH_{Ar}), 130.4 (CH), 148.7 (C) ppm.

6-(Pyrimidin-2-ylamino)hexan-2-one (12f): Compound **12f** was prepared according to the method described in the General Methods and Instruments Section and was purified by flash column chromatography (SiO_2, EtOAc/cyclohexane) to afford a colorless oil. Yield: (Table 1). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.64 (m, 4 H, CH_2), 2.13 (s, 3 H, CH_3), 2.48 (t, *J* = 7.0 Hz, 2 H, CH_2), 3.41 (q, *J* = 6.5 Hz, 2 H, CH_2), 5.24 (br. s, 1 H, NH), 6.51 (dt, *J* = 0.7, *J* = 4.8 Hz, 1 H, CH_{Ar}), 8.26 (d, *J* = 4.8 Hz, 2 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.0 (CH_2), 29.1 (CH_2), 30.0 (CH_3), 41.1 (CH_2), 43.2 (CH_2), 110.4 (CH_{Ar}), 158.0 (CH_{Ar}), 162.3 (C), 208.7 (C) ppm. IR (ATR): ṽ = 3273, 2936, 2864, 1712, 1587, 1533, 1454, 1365, 1164, 802 cm^{-1}. MS (EI, 70 eV, room temperature): *m*/*z* (%) = 193 (20) [M^+], 150 (15), 122 (22), 108 (100), 95 (12), 79 (7). HRMS: calcd. for $C_{10}H_{13}N_3O$ 193.1215; found 193.1213.

6-(4-Nitrophenylamino)-hexan-2-one (12g): Compound **12g** was prepared according to the method described in the General Methods and Instruments Section and was purified by flash column chromatography (SiO_2, cyclohexane/EtOAc, 3:1) to afford yellow crystals. Yield: (Table 1). M.p. 87 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.67 (m, 4 H, CH_2), 2.16 (s, 3 H, CH_3), 2.52 (t, *J* = 6.6 Hz, 2 H, CH_2), 3.21 (t, *J* = 6.6 Hz, 2 H, CH_2), 4.69 (br. s, 1 H, NH), 6.2 (m, 2 H, CH_{Ar}), 8.08 (m, 2 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.7 (CH_2), 28.4 (CH_2), 30.1 (CH_3), 42.9 (CH_2), 43.1 (CH_2), 110.9 (CH_{Ar}), 126.5 (CH_{Ar}), 137.9 (C), 153.3 (C), 208.5 (C) ppm. IR (ATR): ṽ = 3380, 3362, 2945, 1711, 1600, 1465, 1299, 1277, 1109, 832, 754 cm^{-1}. MS (EI, 70 eV, 80 °C): *m*/*z* (%) = 236 (21) [M^+], 202 (17), 151 (100), 105 (25), 84 (41). HRMS: calcd. for $C_{12}H_{16}N_2O_3$ 236.1161; found 236.1153. $C_{12}H_{16}N_2O_3$ (236.27): calcd. C 61.00, H 6.83, N 11.86; found C 61.08, H 6.74, N 11.74.

X-ray Crystallographic Studies of 2–7: Crystals of **2** were obtained from hexane. Crystals of **3**–**6** were grown from toluene/pentane or toluene/hexane. A suitable crystal was covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the –73 °C cold stream of a Stoe IPDS II. Crystals of **3** were measured at room temperature on a Bruker Smart 1000 CCD diffractometer. Subsequent computations were carried out on an Intel Pentium IV PC. All structures were solved by the direct methods (SHELXS-97[44]). The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F* with the program SHELXL-97, by minimizing the function $(F_o - F_c)^2$, where the weight is defined as $4F_o^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes.[44] Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon atom to which they are bonded. The hydrogen atom contributions were calculated, but not refined. The final values of refinement parameters are given in Table 3. The

Table 3. Crystallographic details of **3**–**7**.[a]

	3	**4**	**5**	**6**	**7**
Formula	$C_{24}H_{32}N_2Zn$	$C_{20}H_{24}N_2O_2Zn$	$C_{38}H_{42}N_4O_4Zn$	$C_{30}H_{54}N_4Si_2Zn$	$C_{34}H_{49}F_3N_2O_4SZn$
Formula weight	413.9	389.78	684.13	592.32	704.18
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a [Å]	8.8435(2)	14.4626(12)	20.813(4)	11.3829(8)	12.329(3)
b [Å]	32.1619(9)	8.1213(4)	9.018(2)	10.3885(6)	13.596(3)
c [Å]	16.7764(4)	17.7717(13)	18.049(4)	28.832(2)	21.531(4)
β [°]	104.9290(10)	113.536(6)	90.21(3)	101.408(5)	90.35(3)
V [Å^3]	4610.5(2)	1913.7(2)	3387.4(12)	3342.0(4)	3609.0(13)
Z	8	4	4	4	4
Density [$g cm^{-3}$]	1.193	1.353	1.341	1.177	1.296
Radiation	MoK_α (λ = 0.71073 Å)	MoK_α (λ = 0.71073 Å)	MoK_α (λ = 0.71073 Å)	MoK_α (λ = 0.71073 Å)	MoK_α (λ = 0.71073 Å)
μ [mm^{-1}]	1.075	1.298	0.771	0.830	0.791
Absorption correction	none	Integration (X-Shape)	Integration (X-Shape)	Integration (X-Shape)	none
Reflections collected	21524	13200	18953	17286	25135
Unique reflections	5808 [R_{int} = 0.1133]	5101 [R_{int} = 0.0256]	8907 [R_{int} = 0.0646]	8587 [R_{int} = 0.0634]	6866 [R_{int} = 0.0488]
Observed reflections	4338	4277	5781	5513	6054
Data/parameters	5808/505	5101/229	8907/432	8587/345	6866/413
R_1[b]; wR_2[c]	0.0464; 0.0977	0.0354; 0.0996	0.0442; 0.1082	0.0443; 0.0843	0.0488; 0.1298

[a] All data collected at 203 K. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited. CCDC-739815, -739816, -739817, -739818, -739819 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] P. H. Martinez, K. C. Hultzsch, F. Hampel, *Chem. Commun.* **2006**, 2221–2223.

[2] a) M. C. Wood, D. C. Leitch, C. S. Yeung, J. A. Kozak, L. L. Schafer, *Angew. Chem.* **2007**, *119*, 358-362; *Angew. Chem. Int. Ed.* **2007**, *46*, 354–358; b) L. T. Kaspar, B. Fingerhut, L. Ackermann, *Angew. Chem.* **2005**, *117*, 6126-6128; *Angew. Chem. Int. Ed.* **2005**, *44*, 5972–5974; c) A. Heutling, F. Pohlki, I. Bytschkov, S. Doye, *Angew. Chem.* **2005**, *117*, 3011-3013; *Angew. Chem. Int. Ed.* **2005**, *44*, 2951–2954; d) C. Cao, Y. Li, Y. Shi, A. L. Odom, *Chem. Commun.* **2004**, 2002–2003; e) K. Weitershaus, B. D. Ward, R. Kubiak, C. Müller, H. Wadepohl, S. Doye, L. H. Gade, *Dalton Trans.* **2009**, 4586–4602; f) L. Ackermann, L. T. Kaspar, A. Althammer, *Org. Biomol. Chem.* **2007**, *5*, 1975–1978; g) H. Kim, P. H. Lee, T. Livinghouse, *Chem. Commun.* **2005**, 5205–5207; h) H. Kim, T. Livinghouse, P. H. Lee, *Tetrahedron* **2008**, *64*, 2525–2529; i) P. D. Knight, I. Munslow, P. N. O'Shaughnessy, P. Scott, *Chem. Commun.* **2004**, 894–895; j) E. Smolensky, M. Kapon, M. S. Eisen, *Organometallics* **2007**, *26*, 4510–4527; k) D. A. Watson, M. Chiu, R. G. Bergman, *Organometallics* **2006**, *25*, 4731–4733; l) N. Vujkovic, B. D. Ward, A. Maisse-Francois, H. Wadepohl, P. Mountford, L. H. Gade, *Organometallics* **2007**, *26*, 5522–5534.

[3] a) V. P. Conticello, L. Brard, M. A. Giardello, Y. Tsuji, M. Sabat, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 2761–2762; b) D. Stern, M. Sabat, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 9558–9575; c) C. M. Haar, C. L. Stern, T. J. Marks, *Organometallics* **1996**, *15*, 1765–1784; d) P. W. Roesky, U. Deninger, C. L. Stern, T. J. Marks, *Organometallics* **1997**, *16*, 4486–4492.

[4] a) M. R. Gagne, T. J. Marks, *J. Am. Chem. Soc.* **1989**, *111*, 4108–4109; b) M. R. Gagne, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1992**, *114*, 275–294; c) Y. Li, T. J. Marks, *J. Am. Chem. Soc.* **1996**, *118*, 9295–9306; d) P. W. Roesky, C. L. Stern, T. J. Marks, *Organometallics* **1997**, *16*, 4705–4711; e) Y. Li, T. J. Marks, *J. Am. Chem. Soc.* **1998**, *120*, 1757–1771; f) V. M. Arredondo, F. E. McDonald, T. J. Marks, *J. Am. Chem. Soc.* **1998**, *120*, 4871–4872; g) V. M. Arredondo, F. E. McDonald, T. J. Marks, *J. Am. Chem. Soc.* **1999**, *121*, 3633–3639; h) S. Hong, T. J. Marks, *J. Am. Chem. Soc.* **2002**, *124*, 7886–7887; i) J. S. Ryu, G. Y. Li, T. J. Marks, *J. Am. Chem. Soc.* **2003**, *125*, 12584–12605; j) S. Hong, S. Tian, M. V. Metz, T. J. Marks, *J. Am. Chem. Soc.* **2003**, *125*, 14768–14783.

[5] a) Y. K. Kim, T. Livinghouse, J. E. Bercaw, *Tetrahedron Lett.* **2001**, *42*, 2933–2935; b) Y. K. Kim, T. Livinghouse, *Angew. Chem.* **2002**, *114*, 3797-3799; *Angew. Chem. Int. Ed.* **2002**, *41*, 3645–3647; c) Y. K. Kim, T. Livinghouse, Y. Horino, *J. Am. Chem. Soc.* **2003**, *125*, 9560–9561; d) P. N. O'Shaughnessy, P. D. Knight, C. Morton, K. M. Gillespie, P. Scott, *Chem. Commun.* **2003**, 1770–1771; e) D. V. Gribkov, K. C. Hultzsch, F. Hampel, *Chem. Eur. J.* **2003**, *9*, 4796–4810; f) K. C. Hultzsch, D. V. Gribkov, *Chem. Commun.* **2004**, 730–731; g) K. C. Hultzsch, F. Hampel, T. Wagner, *Organometallics* **2004**, *23*, 2601–2612; h) D. V. Gribkov, K. C. Hultzsch, F. Hampel, *J. Am. Chem. Soc.* **2006**, *128*, 3748–3759; i) D. Riegert, J. Collin, A. Medour, E. Schulz, A. Trifonov, *J. Org. Chem.* **2006**, *71*, 2514–2517.

[6] a) M. R. Bürgstein, H. Berberich, P. W. Roesky, *Organometallics* **1998**, *17*, 1452–1454; b) M. R. Bürgstein, H. Berberich, P. W. Roesky, *Chem. Eur. J.* **2001**, *7*, 3078–3085; c) A. Zulys, T. K. Panda, M. T. Gamer, P. W. Roesky, *Chem. Commun.* **2004**, 2584–2585; d) A. Zulys, T. K. Panda, M. T. Gamer, P. W. Roesky, *Organometallics* **2005**, *24*, 2197–2202; e) M. Rastätter, A. Zulys, P. W. Roesky, *Chem. Commun.* **2006**, 874–876; f) M. Rastätter, A. Zulys, P. W. Roesky, *Chem. Eur. J.* **2007**, *13*, 3606–3616.

[7] Rh: a) C. Alonso-Moreno, F. Carrillo-Hermosilla, J. Romero-Fernandez, A. M. Rodriguez, A. Otero, A. Antinolo, *Adv. Synth. Catal.* **2009**, *351*, 881–890; b) C. Baudequin, J.-J. Brunet, M. Rodriguez-Zubiri, *Organometallics* **2007**, *26*, 5264–5266; c) E. B. Bauer, G. T. S. Andavan, T. K. Hollis, R. J. Rubio, J. Cho, G. R. Kuchenbeiser, T. R. Helgert, C. S. Letko, F. S. Tham, *Org. Lett.* **2008**, *10*, 1175–1178; d) S. Burling, L. D. Field, B. A. Messerle, P. Turner, *Organometallics* **2004**, *23*, 1714–1721; e) L. D. Field, B. A. Messerle, K. Q. Vuong, P. Turner, *Dalton Trans.* **2009**, 3599–3614; f) L. D. Field, B. A. Messerle, K. Q. Vuong, P. Turner, T. Failes, *Organometallics* **2007**, *26*, 2058–2069; g) Y. Fukumoto, H. Asai, M. Shimizu, N. Chatani, *J. Am. Chem. Soc.* **2007**, *129*, 13792–13793; h) Z. Liu, J. F. Hartwig, *J. Am. Chem. Soc.* **2008**, *130*, 1570–1571; i) A. Takemiya, J. F. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 6042–6043; j) M. Utsunomiya, R. Kuwano, M. Kawatsura, J. F. Hartwig, *J. Am. Chem. Soc.* **2003**, *125*, 5608–5609. Pd: k) L. Ackermann, R. Sandmann, M. V. Kondrashov, *Synlett* **2009**, 1219–1222; l) B. M. Cochran, F. E. Michael, *J. Am. Chem. Soc.* **2008**, *130*, 2786–2792; m) B. M. Cochran, F. E. Michael, *Org. Lett.* **2008**, *10*, 329–332; n) O. Jimenez, T. E. Mueller, C. Sievers, A. Spirkl, J. A. Lercher, *Chem. Commun.* **2006**, 2974–2976; o) A. M. Johns, Z. Liu, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2007**, *46*, 7259–7261; p) A. M. Johns, M. Utsunomiya, C. D. Incarvito, J. F. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 1828–1839; q) K. Li, K. K. Hii, *Chem. Commun.* **2003**, 1132–1133; r) L. M. Lutete, I. Kadota, Y. Yamamoto, *J. Am. Chem. Soc.* **2004**, *126*, 1622–1623; s) F. E. Michael, B. M. Cochran, *J. Am. Chem. Soc.* **2006**, *128*, 4246–4247; t) S. Qiu, Y. Wei, G. Liu, *Chem. Eur. J.* **2009**, *15*, 2751–2754; u) N. Sakai, A. Ridder, J. F. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 8134–8135; v) A. R. Shaffer, J. A. R. Schmidt, *Organometallics* **2008**, *27*, 1259–1266; w) M. Utsunomiya, J. F. Hartwig, *J. Am. Chem. Soc.* **2003**, *125*, 14286–14287. Pt: x) C. F. Bender, W. B. Hudson, R. A. Widenhoefer, *Organometallics* **2008**, *27*, 2356–2358; y) C. F. Bender, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2005**, *127*, 1070–1071; z) J.-J. Brunet, M. Cadena, N. C. Chu, O. Diallo, K. Jacob, E. Mothes, *Organometallics* **2004**, *23*, 1264–1268; aa) J.-J. Brunet, N. C. Chu, O. Diallo, *Organometallics* **2005**, *24*, 3104–3110; J.-J. Brunet, N.-C. Chu, M. Rodriguez-Zubiri, *Eur. J. Inorg. Chem.* **2007**, 4711–4722; ac) D. Karshtedt, A. T. Bell, T. D. Tilley, *J. Am. Chem. Soc.* **2005**, *127*, 12640–12646; ad) M. R. Reithofer, M. Galanski, V. B. Arion, B. K. Keppler, *Chem. Commun.* **2008**, 1091–1093.

[8] a) M. R. Crimmin, I. J. Caseley, M. S. Hill, *J. Am. Chem. Soc.* **2005**, *127*, 2042–2043; b) M. Arrowsmith, M. S. Hill, G. Kociok-Kohn, *Organometallics* **2009**, *28*, 1730–1738; c) A. G. M. Barrett, T. C. Boorman, M. R. Crimmin, M. S. Hill, G. Kociok-Kohn, P. A. Procopiou, *Chem. Commun.* **2008**, 5206–5208; d) A. G. M. Barrett, I. J. Casely, M. R. Crimmin, M. S. Hill, J. R. Lachs, M. F. Mahon, P. A. Procopiou, *Inorg. Chem.* **2009**, *48*, 4445–4453; e) J. R. Lachs, A. G. M. Barrett, M. R. Crimmin, G. Kociok-Kohn, M. S. Hill, M. F. Mahon, P. A. Procopiou, *Eur. J. Inorg. Chem.* **2008**, 4173–4179; f) S. Datta, P. W. Roesky, S. Blechert, *Organometallics* **2007**, *26*, 4392–4394.

[9] J. G. Taylor, N. Whittall, K. K. Hii, *Org. Lett.* **2006**, *8*, 3561–3564.

[10] J. Sun, S. A. Kozmin, *Angew. Chem.* **2006**, *118*, 5113-5115; *Angew. Chem. Int. Ed.* **2006**, *45*, 4991–4993.

[11] a) C. Brouwer, C. He, *Angew. Chem.* **2006**, *118*, 1776-1779; *Angew. Chem. Int. Ed.* **2006**, *45*, 1744–1747; b) X. Han, R. A. Widenhoefer, *Angew. Chem.* **2006**, *118*, 1779-1781; *Angew. Chem. Int. Ed.* **2006**, *45*, 1747–1749; c) Z. Zhang, C. Liu, R. E. Kinder, X. Han, H. Qian, R. A. Widenhoefer, *J. Am. Chem.*

Soc. **2006**, *128*, 9066–9073; d) J. E. Kang, H. B. Kim, J. W. Lee, S. Shin, *Org. Lett.* **2006**, *8*, 3537–3540; e) N. Nishina, Y. Yamamoto, *Synlett* **2007**, 1767–1770; f) J. Zhang, C.-G. Yang, C. He, *J. Am. Chem. Soc.* **2006**, *128*, 1798–1799; g) Y. Zhang, J. P. Donahue, C.-J. Li, *Org. Lett.* **2007**, *9*, 627–630; h) Z. Zhang, S. D. Lee, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2009**, *131*, 5372–5373.

[12] T. E. Müller *in Encyclopedia of Catalysis* (Ed.: J. T. Horváth), Wiley, New York, **2002**.

[13] Recent reviews: a) D. M. Roundhill, *Chem. Rev.* **1992**, *92*, 1–27; b) T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675–703; c) M. Johannsen, K. A. Jørgensen, *Chem. Rev.* **1998**, *98*, 1689–1708; d) M. Nobis, B. Drießen-Hölscher, *Angew. Chem.* **2001**, *113*, 4105-4108; *Angew. Chem. Int. Ed.* **2001**, *40*, 3983–3985; e) J.-J. Brunet, D. Neibecker in *Catalytic Heterofunctionalization* (Eds.: A. Togni, H. Grützmacher), VCH Weinheim. **2001**, pp. 91–141; f) J. Seayad, A. Tillack, C. G. Hartung, M. Beller, *Adv. Synth. Catal.* **2002**, *344*, 795–813; g) F. Pohlki, S. Doye, *Chem. Soc. Rev.* **2003**, *32*, 104–114; h) I. Bytschkov, S. Doye, *Eur. J. Org. Chem.* **2003**, 935–946; i) P. W. Roesky, T. E. Müller, *Angew. Chem.* **2003**, *115*, 2812-2814; *Angew. Chem. Int. Ed.* **2003**, *42*, 2708–2710; j) J. F. Hartwig, *Pure Appl. Chem.* **2004**, *76*, 507–516; k) S. Hong, T. J. Marks, *Acc. Chem. Res.* **2004**, *37*, 673–686; l) K. C. Hultzsch, *Adv. Synth. Catal.* **2005**, *347*, 367–391; m) I. Aillaud, J. Collin, J. Hannedouche, E. Schulz, *Dalton Trans.* **2007**, 5105–5118; n) T. E. Müller, K. C. Hultzsch, M. Yus, F. Foubelo, M. Tada, *Chem. Rev.* **2008**, *108*, 3795–3892.

[14] E. Nakamura in *Organometallics in Synthesis* – A. Manual (Eds.: M. Schlosser), John Wiley & Sons, Ltd, Chichester, **2002**, pp. 579–664.

[15] a) A. Zulys, M. Dochnahl, D. Hollmann, K. Löhnwitz, J.-S. Herrmann, P. W. Roesky, S. Blechert, *Angew. Chem.* **2005**, *117*, 7972-7976; *Angew. Chem. Int. Ed.* **2005**, *44*, 7794–7798; b) M. Dochnahl, Ph. D. Thesis, *Technische Universität Berlin*, Germany, **2007**.

[16] a) N. Meyer, K. Löhnwitz, A. Zulys, P. W. Roesky, M. Dochnahl, S. Blechert, *Organometallics* **2006**, *25*, 3730–3734; b) M. Dochnahl, K. Löhnwitz, J.-W. Pissarek, P. W. Roesky, S. Blechert, *Dalton Trans.* **2008**, 2844–2848.

[17] a) M. Dochnahl, J.-W. Pissarek, S. Blechert, K. Löhnwitz, P. W. Roesky, *Chem. Commun.* **2006**, 3405–3407; b) M. Dochnahl, K. Löhnwitz, J.-W. Pissarek, M. Biyikal, S. Schulz, S. Schön, N. Meyer, P. W. Roesky, S. Blechert, *Chem. Eur. J.* **2007**, *13*, 6654–6666.

[18] J. E. Parks, R. H. Holm, *Inorg. Chem.* **1968**, *7*, 1408–1416.

[19] S. G. McGeachin, *Can. J. Chem.* **1968**, *46*, 1903–1912.

[20] C. L. Honeybourne, G. A. Webb, *Chem. Commun. (London)* **1968**, 739–740.

[21] M. F. Lappert, D.-S. Liu, *J. Organomet. Chem.* **1995**, *500*, 203–217.

[22] J. Feldman, S. J. McLain, A. Parthasarathy, W. J. Marshall, J. C. Calabrese, S. D. Arthur, *Organometallics* **1997**, *16*, 1514–1516.

[23] W. K. Kim, M. J. Fevola, L. M. Liable-Sands, A. L. Rheingold, K. H. Theopold, *Organometallics* **1998**, *17*, 4541–4543.

[24] V. C. Gibson, P. J. Maddox, C. Newton, C. Redshaw, G. A. Solan, A. J. P. White, D. J. Williams, *Chem. Commun.* **1998**, 1651–1652.

[25] R. Vollmerhaus, M. Rahim, R. Tomaszewski, S. Xin, N. J. Taylor, S. Collins, *Organometallics* **2000**, *19*, 2161–2169.

[26] M. F. Pilz, C. Limberg, B. B. Lazarov, K. C. Hultzsch, B. Ziemer, *Organometallics* **2007**, *26*, 3668–3676.

[27] M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **1998**, *120*, 11018–11019.

[28] M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 8738–8749.

[29] D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates, *Angew. Chem.* **2002**, *114*, 2711-2714; *Angew. Chem. Int. Ed.* **2002**, *41*, 2599–2602.

[30] D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2003**, *125*, 11911–11924.

[31] M. Cheng, A. B. Attygalle, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **1999**, *121*, 11583–11584.

[32] B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238.

[33] L. R. Rieth, D. R. Moore, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 3473–3477.

[34] R. Eberhardt, M. Allmendinger, G. A. Luinstra, B. Rieger, *Organometallics* **2003**, *22*, 211–214.

[35] R. Eberhardt, M. Allmendinger, M. Zintl, C. Troll, G. A. Luinstra, B. Rieger, *Macromol. Chem. Phys.* **2004**, *205*, 42–47.

[36] a) S. Gong, H. Ma, *Dalton Trans.* **2008**, 3345–3357; b) D. T. Carey, E. K. Cope-Eatough, E. Vilaplana-Mafé, F. S. Mair, R. G. Pritchard, J. E. Warren, R. J. Woods, *Dalton Trans.* **2003**, 1083–1093.

[37] M. Cheng, N. A. Darling, E. B. Lobkovsky, G. W. Coates, *Chem. Commun.* **2000**, 2007–2008.

[38] a) H. G. Müller, K. Hartke, *Arch. Pharm. (Weinheim)* **1988**, *321*, 879–884; b) H. B. Ammar, M. T. Kaddachi, P. H. Kahn, *Phys. Chem. News* **2003**, *9*, 137–139.

[39] E. H. Schweizer, F. Märki, C. Lehmann, H. Dietrich, *J. Med. Chem.* **1983**, *26*, 964–973.

[40] J. Prust, A. Stasch, W. Zheng, H. W. Roesky, E. Alexopoulus, I. Uson, D. Böhler, T. Schuchardt, *Organometallics* **2001**, *20*, 3825–3828.

[41] L. A. Gayler, G. Wilkinson, *Inorg. Synth.* **1997**, *19*, 253–257.

[42] a) L. Ackermann, A. Althammer, *Synlett* **2008**, *7*, 995–998; b) L. Ackermann, L. T. Kaspar, A. Althammer, *Org. Biomol. Chem.* **2007**, *5*, 1975–1978; c) D. C. Rosenfeld, S. Shekhar, A. Takemiya, M. Utsunomiya, J. F. Hartwig, *Org. Lett.* **2006**, *8*, 4179–4182; d) L. L. Anderson, J. Arnold, R. G. Bergman, *J. Am. Chem. Soc.* **2005**, *127*, 14542–14543.

[43] a) K. Alex, A. Tillack, N. Schwarz, M. Beller, *ChemSusChem* **2008**, *1*, 333–338; b) J. Bódis, T. E. Müller, J. A. Lercher, *Green Chem.* **2003**, *5*, 227–231; c) T. H. Müller, M. Grosche, E. Herdtweck, A.-K. Pleier, E. Walter, Y.-K. Yan, *Organometallics* **2000**, *19*, 170–183.

[44] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

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