DOI: 10.1002/ejic.200800905

Aminotroponiminate Zinc Complexes with Different Leaving Groups as Catalysts for the Intramolecular Hydroamination of Alkenes

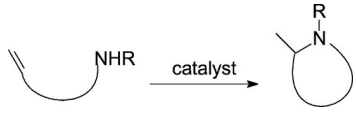
Karolin Löhnwitz,[a] Matthias J. Molski,[a] Anja Lühl,[b] Peter W. Roesky,*[b] Maximilian Dochnahl,[c] and Siegfried Blechert*[c]

Keywords: Homogeneous catalysis / Heterocycles / Hydroamination / N ligands / Zinc / Organozinc compounds

The (aminotroponiminato)phenylzinc complexes {*N*-isopropyl-2-(isopropylamino)troponiminato}phenylzinc, [{ATI(iPr)$_2$}-ZnPh], {*N*-isopropyl-2-(isopropylamino)-5-(phenylsulfanyl)-troponiminato}phenylzinc, [{PhS-ATI(iPr)$_2$}ZnPh], {*N*-cyclohexyl-2-(cyclohexylamino)troponiminato}phenylzinc, [{ATI-(Cy)$_2$}ZnPh] and the corresponding bis(trimethylsilyl)amido compounds [{ATI(iPr)$_2$}ZnN(SiMe$_3$)$_2$], [{PhS-ATI(iPr)$_2$}ZnN-(SiMe$_3$)$_2$], and [{ATI(Cy)$_2$}ZnN(SiMe$_3$)$_2$] were prepared and fully characterized. These compounds were obtained by reaction of the corresponding aminotroponimines with ZnPh$_2$ and [Zn{N(SiMe$_3$)$_2$}$_2$], respectively. The new complexes were compared with the corresponding methylzinc complexes, which were previously reported, to study the influence of the substituents of the zinc atom in the catalytic hydroamination/cyclization reaction. In the presence of equimolar amounts of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] it was shown that the methyl und phenyl compounds show comparable activities, while those bearing a bis(trimethylsilyl)amido group are significantly slower. Obviously the size of the leaving group and the nature of the formed by-product have a significant influence on the reaction rate.

Introduction

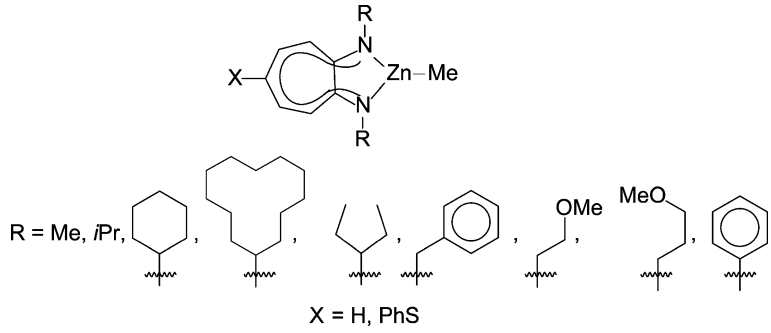
In contrast to its heavier congeners zinc is biologically one of the most important metals. The body of an adult human contains about 2 g of zinc.[1] As a result of these properties zinc is a predestined metal for the synthesis of biological and pharmaceutical relevant molecules. The first zinc compounds were already discovered in 1849 by Sir Edward Frankland.[2] After their discovery in 1900, Grignard[3] and later on organolithium reagents superseded alkylzinc compounds in organic synthesis[4] because they show a higher nucleophilic reactivity compared to zinc reagents.[5] About 30 years ago it was realized that the low nucleophilic reactivity of organozinc compounds can be used to prepare functionalized organozinc reagents.[6] Today, numerous catalytic and stoichiometric zinc-mediated organic reactions such as the Negishi cross coupling, the Simmons–Smith cyclopropanation, the Reformatsky reaction, the CO_2/epoxide copolymerisation and a number of nucleophilic addition and substitution reactions are known.[7] Recently we introduced organozinc complexes as catalysts for the intramolecular hydroamination reaction, which is the direct addition of N–H bonds to C–C multiple bonds (Scheme 1).[8]



Scheme 1. Intramolecular hydroamination of amino olefins.

A number of metals and catalysts has been employed for this transformation, especially the lanthanides[,[8c,8d,9] group 4 metals,[10] the platinum metals[11] and also calcium[12] and very recently gold.[8b,13] However, most of these catalysts have disadvantages like high prices, toxicity and/or little tolerance towards polar functional groups. As alternative we recently introduced various aminotroponiminate zinc methyl complexes (Scheme 2) as catalysts for the intramolecular hydroamination.[14] In this context, we investigated the influence of steric modifications of the alkyl groups at the nitrogen atoms of the aminotroponimine ligand[15] and electronic modifications by using aminotroponiminates bearing a phenylsulfanyl group in 5-position of the ligand.[16] We were able to show the major influence of the steric and electronic environment around the zinc atom on both reactivity and stability of the corresponding complexes. The resulting complexes possess interesting advantages compared to other metal catalysts: *i*. they show very high tolerance towards polar functional groups, *ii*. they are remarkably stable towards air and moisture. So far, we focused on aminotroponiminate zinc methyl complexes. Herein, we report on our recent studies on the substitution of the methyl group by aryl and amide moieties and the

[a] Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstraße 34–36, 14195 Berlin, Germany
[b] Institut für Anorganische Chemie, Universität Karlsruhe, Engesserstr. 15, 76128 Karlsruhe, Germany
[c] Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

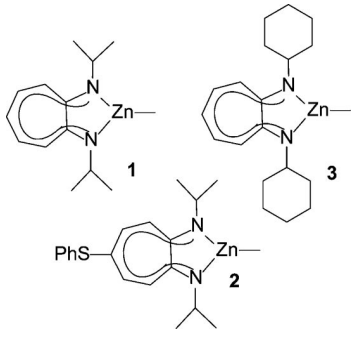


Scheme 2.

catalytic properties of the corresponding (aminotroponiminato)zinc complexes. Now, we are interested to replace the methyl group by arenes and amides to study the influence of these groups onto the catalytic properties.

Results and Discussion

In our previous studies, we could show that the first generation catalysts {*N*-isopropyl-2-(isopropylamino)troponiminato}methylzinc, [{ATI(*i*Pr)$_2$}ZnMe] (**1**), the substituted compound {*N*-isopropyl-2-(isopropylamino)-5-(phenylsulfanyl)troponiminato}methylzinc, [{PhS-ATI(*i*Pr)$_2$}ZnMe] (**2**), and the cyclohexyl derivative {*N*-cyclohexyl-2-(cyclohexylamino)troponiminato}methylzinc, [{ATI(Cy)$_2$}ZnMe] (**3**) (Scheme 3) show the best activities as catalysts for intramolecular hydroamination/cyclization reaction.[15,16] Based on these results we now planed to synthesize the analogue phenylzinc and bis(trimethylsilyl)amide zinc derivatives to study the influence of these groups on the catalytic properties.

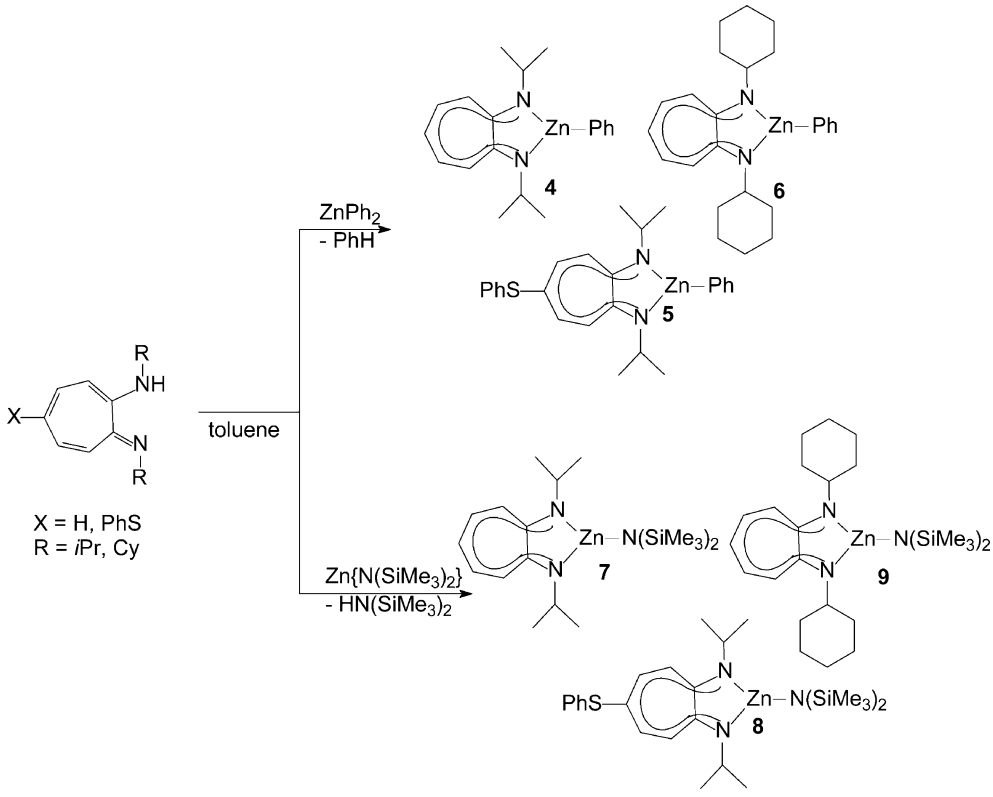


Scheme 3.

The zinc phenyl complexes [{ATI(*i*Pr)$_2$}ZnPh] (**4**), [{PhS-ATI(*i*Pr)$_2$}ZnPh] (**5**), and [{ATI(Cy)$_2$}ZnPh] (**6**) were obtained by the reactions of the neutral ligands with diphenylzinc in toluene at 0 °C (Scheme 4). Compounds **4**–**6** were obtained as yellow crystalline powders. They were characterized by MS, ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H and ^{13}C{^{1}H} NMR spectra show the expected signal set for the aminotroponiminate ligands. The NMR signals for the Ph-Zn group are not very significant. They are slightly shifted upfield/downfield compared to the starting material Ph_2Zn.[17] In general the compounds are volatile and show intense molecular peaks in the MS spectrum.

The structures of compounds **4**–**6** were confirmed by single-crystal X-ray diffraction in the solid-state (see Figures 1, 2, and 3). Compound **4** and **5** crystallize in the monoclinic space group $P2_1/c$ with four molecules of complex in the unit cell. In contrast compound **6** crystallizes in the chiral space group $P2_1$ having two molecules of the metal complex in the unit cell. As already observed for the corresponding aminotroponiminato zinc methyl complexes the zinc atom in all three structures is trigonal-planar coordinated by the phenyl group and the two nitrogen atoms (N1 and N2) of the aminotroponiminate ligands. The observed N–Zn bond lengths [N1–Zn 1.961(2) Å and N2–Zn 1.963(2) Å (**4**); N1–Zn 1.977(2) Å and N2–Zn 1.972(2) Å (**5**), N1–Zn 1.967(2) Å and N2–Zn 1.974(2) Å (**6**)] are in the expected range [e.g. Zn1–N1 1.980(4) Å and Zn1–N2 1.955(4) Å in **1**].[14] The bond lengths between the zinc atom and the carbon atom of the phenyl group [C14–Zn 1.954(2) Å (**4**), C20–Zn 1.952(3) Å (**5**), 1.947(2) Å (**6**)] are also in the same region compared to **1** [1.941(5) Å]. An almost perpendicular orientation of the phenyl group towards the seven-membered ring of the aminotroponiminate ligand is observed. The angles N1–Zn–C20 [139.02(11)° (**5**), 136.87(15)° (**6**)] and N2–Zn1–C20 [137.48(11)° (**5**), 139.70(15)° (**6**)] are close range. The N–Zn–N bit angles are smaller than in a symmetric triangle [N1–Zn–N2 82.86(8)° (**4**), 82.89(9)° (**5**), 83.42(8)° (**6**)].

The bis(trimethylsilyl)amido compounds [{ATI(*i*Pr)$_2$}-ZnN(SiMe$_3$)$_2$] (**7**), [{PhS-ATI(*i*Pr)$_2$}ZnN(SiMe$_3$)$_2$] (**8**), and [{ATI(Cy)$_2$}ZnN(SiMe$_3$)$_2$] (**9**) were obtained in a similar way to the zinc phenyl complexes by the reaction of the corresponding aminotroponimines with [Zn{N(SiMe$_3$)$_2$}$_2$][18] in toluene at 0 °C (Scheme 4). The products were obtained as yellow powders or crystals. The new complexes have been characterized by standard analytical/spectroscopic techniques and the solid-state structures were established by single-crystal X-ray diffraction. The ^{1}H and ^{13}C{^{1}H} NMR spectra show the expected set of signals for the aminotroponiminate ligands and the characteristic sharp singulett for the N(SiMe$_3$)$_2$ group, which occurs in the range of δ = 0.22–0.37 ppm in the ^{1}H NMR spectrum.



Scheme 4.

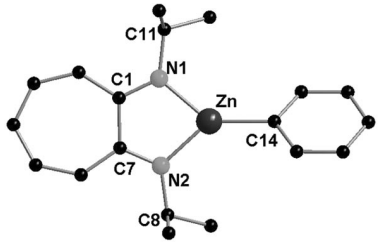


Figure 1. Solid-state structure of **4** showing the atom labeling scheme, omitting hydrogen atoms. Selected distances [Å] and angles [°] given for one of the two independent molecules in the asymmetric unit: N1–Zn 1.961(2), N2–Zn 1.963(2), C1–N1 1.330(3), C14–Zn 1.954(2), C1–C7 1.493(3), C7–N2 1.332(3); N1–Zn–C14 139.78(10), N2–Zn–C14 137.31(10), N1–Zn–N2 82.86(8).

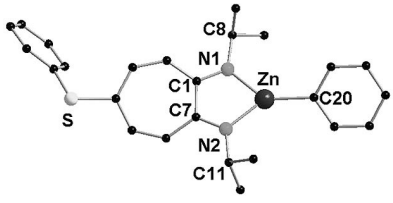


Figure 2. Solid-state structures of **5** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [Å] or angles [°]: N1–Zn 1.977(2), N2–Zn 1.972(2), C20–Zn 1.952(3), C1–N1 1.327(3), C1–C7 1.487(4), C7–N2 1.320(4); N1–Zn–N2 82.89(9), N1–Zn–C20 139.02(11), N2–Zn–C20 137.48(11).

Compounds **7** and **8** crystallize in monoclinic space group $P2_1/c$ having four molecules of the corresponding metal complex in the unit cell (see Figures 4 and 5). In contrast, the structure of compound **9** could be refined as a twin only in triclinic space group $P\bar{1}$. The data collected from **9** were poor and prohibited a full refinement. However the connectivity of **9** and its composition were deduced. In all three structures the zinc atom is trigonal planar coordinated by the nitrogen atom of the bis(trimethylsilyl)amido group and the two nitrogen atoms (N1 and N2) of the aminotroponiminate ligands. Compared to compounds **4**–**6** the increased steric bulk of the bis(trimethylsilyl)amido group does not have a significant influence on the structural parameters. The N–Zn bond lengths of the aminotroponiminate ligands of compounds **7**–**9** [N1–Zn 1.947(7) Å and N2–Zn 1.957(6) Å (**7**), N1–Zn 1.968(3) Å and N2–Zn 1.960(3) Å (**8**)] are in the same range as observed for com-

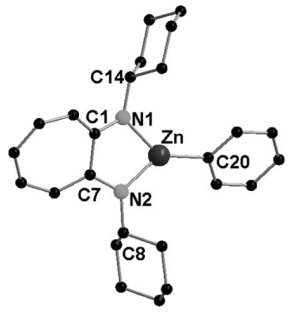


Figure 3. Solid-state structures of **6** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [Å] or angles [°]: N1–Zn 1.967(2), N2–Zn 1.974(2), C20–Zn 1.947(2), C1–N1 1.325(4), C1–C7 1.492(4), C7–N2 1.327(4); N1–Zn–N2 83.42(8), N1–Zn–C20 136.87(15), N2–ZnC20 139.70(15).

pounds **4**–**6**. In contrast, the N–Zn bond length of the bis(trimethylsilyl)amido group is significantly shorter [N3–Zn 1.874(7) Å (**7**), N3–Zn 1.869(3) Å], which is a result of the stronger electrostatic interaction. As a result of the high steric demand of the bis(trimethylsilyl)amido ligand, this group is nearly perpendicularly oriented to the aminotroponiminate ligands. Thus, the torsion angle of e.g. Si1–N3–Zn–N2 is 85.94(2)°.

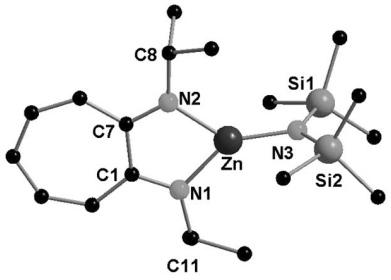


Figure 4. Solid-state structures of **7** showing the atom labeling scheme, hydrogen atoms omitted. Selected bond lengths [Å] or angles [°]: N1–Zn 1.947(7), N2–Zn 1.957(6), N3–Zn 1.874(7), C1–N1 1.340(11), C1–C7 1.469(12), C7–N2 1.342(11); N1–Zn–N2 83.3(3), N1–Zn–N3 139.3(3), N2–Zn–N3 137.2(3).

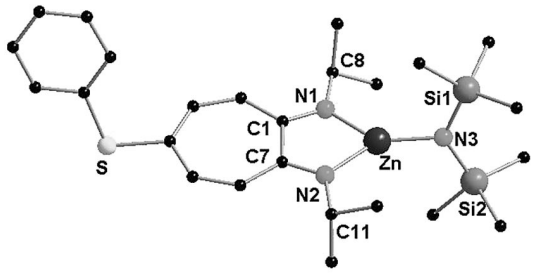
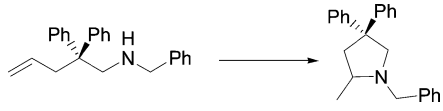


Figure 5. Solid-state structures of **8** showing the atom labeling scheme, hydrogen atoms omitted. Selected bond lengths [Å] or angles [°]: N1–Zn 1.968(3), N2–Zn 1.960(3), N3–Zn 1.869(3), C1–N1 1.324(5), C1–C7 1.502(5), C7–N2 1.329(4); N3–Zn–N2 138.99(12), N3–Zn–N1 137.63(12), N2–Zn–N1 83.29(12).

The new compounds **4**–**9** were used as catalysts for the hydroamination/cyclization of the two non-activated amino olefins β-phenyl-*N*-(phenylmethyl)-β-2-propen-1-yl-benzeneethanamine (Table 1) and *N*-(2,2-diphenyl-4-penten-1-yl)-2-furanmethanamine (Table 2). The new complexes were then compared with the corresponding zinc methyl complexes to study the influence of the substituents of the zinc atom. The reactions were carried out at 80 °C in [D_6]benzene with a catalyst loading of 2.5 mol-% and 2.5 mol-% of [$PhNMe_2H$][$B(C_6F_5)_4$]. The conversions were quantitative in the majority of all of the investigated cases by using the methyl and phenylzinc compounds (see Tables 1 and 2, entries 1–2, 4–5, 7–8). Moreover, having the same aminotroponiminato ligand, the methyl- and phenylzinc catalysts show similar yields after a fixed period of time in the cyclization reactions of the same substrate (e.g. Table 2, entries 1–2, 4–5, and 7–8). The only exception is seen in Table 1 entry 5, which obviously is slower. In contrast, the bis(trimethylsilyl)amido catalysts show in all cases significantly lower yields (see Tables 1 and 2, entries 3, 6, 9). We suggest, that the phenyl and methyl compounds form a similar catalytic active species in solution by the addition of one equivalent of [$PhNMe_2H$][$B(C_6F_5)_4$]. It has previously been shown that this has a beneficial effect on the reactivity of the zinc catalyst.[14] We attribute this to the formation of a cationic zinc species, which is formed by the protonolysis of the Zn–R moiety. The disappearance of the Zn–R group has been monitored by ^{1}H NMR spectroscopy. The thus formed by product, methane and benzene, respectively, are inert and obviously are not involved in any kind of back reaction. In contrast, the bis(trimethylsilyl)amido group forms bis(trimethylsilyl)amine as byproduct. The Lewis-basic amine is not inert and can coordinate to the catalytic active species thus hampering the catalytic activity. This was supported by a control experiments, in which $HN(SiMe_3)_2$ was added to the reaction shown in Table 2, entry 1. A significant increase in reaction time was observed. Moreover, as a result of the higher steric demand of the bis(trimethylsilyl)amido group a slower protonolysis of this group at the beginning of the reaction may be anticipated. Under the used reaction conditions the cocatalysts [$PhNMe_2H$]-[$B(C_6F_5)_4$] does not show any activity for primary amines. Using β-phenyl-*N*-(phenylmethyl)-β-2-propen-1-yl-benzeneethanamine as substrate (Table 1) a 94% conversion was observed after 20 h showing a sluggish reactivity of the cocatalyst alone for this substrate. In the case of the slow bis(trimethylsilyl)amine catalysts (e.g. Table 1, entries 6 and 9) the rates may be influenced by the activity of the cocatalyst.

Table 1. Cyclization of β-phenyl-*N*-(phenylmethyl)-β-2-propen-1-yl-benzeneethanamine.[a]

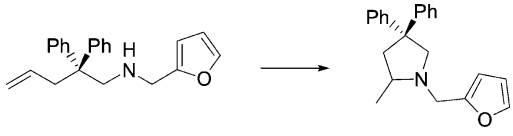


Entry[a]	Catalyst	time [min]	% Conv.[b]
1	[{ATI(*i*Pr)$_2$}ZnMe] (**1**)	95	quant. 99[c]
2	[{ATI(*i*Pr)$_2$}ZnPh] (**4**)	95	92
3	[{ATI(*i*Pr)$_2$}Zn{N(SiMe$_3$)$_2$}] (**7**)	95	29
4	[{ATI(Cy)$_2$}ZnMe] (**2**)	20	quant.
5	[{ATI(Cy)$_2$}ZnPh] (**5**)	60	quant.
6	[{ATI(Cy)$_2$}Zn{N(SiMe$_3$)$_2$}] (**8**)	720	64
7	[{PhS-ATI(*i*Pr)$_2$}ZnMe] (**3**)	40	quant. 93[c]
8	[{PhS-ATI(*i*Pr)$_2$}ZnPh] (**6**)	40	quant.
9	[{PhS-ATI(*i*Pr)$_2$}Zn{N(SiMe$_3$)$_2$}] (**9**)	720	87

[a] Reaction conditions: 2.5 mol-% cat. 2.5 mol-% [$PhNMe_2H$]-[$B(C_6F_5)_4$] in 0.5 mL of C_6D_6 at 80 °C. [b] Determined by ^{1}H NMR spectroscopy. [c] Isolated yield.

Our observations are supported by a recent publication of Doye et al. who studied titanium complexes of composition [{η^5-(C_5H_4)-$SiMe_2$-N*t*Bu}TiX_2] (X = NMe_2, Me, Cl) as catalyst precursors for the intermolecular hydroamination of alkynes and the intramolecular hydroamination of alkenes.[19] Their results strongly suggested that the catalytically active species are identical for reactions performed with the bis(dimethylamido) and the dimethyl complex. Under their reaction conditions, the leaving groups NMe_2 and

Table 2. Cyclization of [(2,2-diphenylpent-4-enyl)furan-2-yl]methylamine.[a]



Entry[a]	Catalyst	Time [h]	% Conv.[b]
1	[{ATI(iPr)$_2$}ZnMe] (**1**)	6	quant.
2	[{ATI(iPr)$_2$}ZnPh] (**4**)	6	quant.
3	[{ATI(iPr)$_2$}Zn{N(SiMe$_3$)$_2$}] (**7**)	30	70%
4	[{ATI(Cy)$_2$}ZnMe] (**2**)	2.5	quant. 94[c]
5	[{ATI(Cy)$_2$}ZnPh] (**5**)	2.5	quant.
6	[{ATI(Cy)$_2$}Zn{N(SiMe$_3$)$_2$}] (**8**)	30	quant.
7	[{PhS-ATI(iPr)$_2$}ZnMe] (**3**)	4	quant. 96[c]
8	[{PhS-ATI(iPr)$_2$}ZnPh] (**6**)	4	quant.
9	[{PhS-ATI(iPr)$_2$}Zn{N(SiMe$_3$)$_2$}] (**9**)	29	quant.

[a] Reaction conditions: 2.5 mol-% cat. 2.5 mol-% [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] in 0.5 mL of C$_6$D$_6$ at 80 °C. [b] Determined by ^{1}H NMR spectroscopy. [c] Isolated yield.

Me are protolytically removed by the reacting amine to form catalytically active imido or amido complexes, together with dimethylamine or methane. The preparative and kinetic studies clearly indicated that dimethylamine, which is formed from the [{η^5-(C$_5$H$_4$)-SiMe$_2$-NtBu}Ti(NMe$_2$)] catalyst precursor and the reacting amine, was able to convert the catalytically active imido or amido complexes back into the catalyst precursor and therefore inhibits the reactions.

Summary

In summary, we have prepared and fully characterized six different (aminotroponiminato)phenylzinc and bis(trimethylsilyl)amido complexes. All of them were characterized by single X-ray diffraction. The new compounds were then used as catalysts for the hydroamination/cyclization of two non-activated olefins bearing different functional groups. The new complexes were compared with the corresponding methylzinc complexes that have previously been prepared in order to study the influence of the substituents of the ligands in the catalytic hydroamination/cyclization reaction. It was shown that the methyl und phenylzinc compounds show comparable activities in the presence of equimolar amounts of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$], while the bis(trimethylsilyl)amido are significantly slower. Obviously, the size of the leaving group and the nature of the formed byproduct have a significant influence on the reaction rate.

Experimental Section

General: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-4} Torr) line, or in an argon-filled MBraun glove box. Tetrahydrofuran was predried with Na wire and distilled under nitrogen from Na/K benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from LiAlH$_4$. All solvents for vacuum line manipulations were stored in vacuo over LiAlH$_4$ in resealable flasks. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft mbH or Euriso-Top GmbH (all solvents contained at least 99 atom-% D) and were dried, degassed, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded on a Jeol JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Mass spectra were recorded at 70 eV on Varian MAT 711. IR spectra were obtained on a Shimadzu FTIR-8400s. Elemental analyses were carried out with an Elementar vario EL III. [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] was purchased from Strem. ZnMe$_2$ was obtained from Aldrich. Aminoalkenes were prepared using modified literature procedures[11b,15b] from commercially available starting materials from Aldrich, Acros Organics and Fluka. Prior to use, all substrates were purified either by distillation or recrystallization. 2-(*N*-Isopropylamino)tropone,[20] Ph$_2$Zn,[17] [Zn{N(SiMe$_3$)$_2$}$_2$],[18] *N*-isopropyl-2-(isopropylamino)-5-(phenylsulfanyl)troponimine,[16] and *N*-cyclohexyl-2-(cyclohexylamino)troponiminate[15] were prepared according to literature procedures.

General Procedure for the Synthesis of [{R^1-ATI(R^2)$_2$}ZnPh] 4–6: A solution of the aminotroponimine in toluene was slowly added to a solution of ZnPh$_2$ in toluene at 0 °C. Then, the solution were slowly warmed to room temperature and stirred for 3 h. Thereafter, the solution was filtered and all volatiles were removed under reduced pressure. The yellow residue was washed twice with *n*-pentane (5 mL).

[{*N*-Isopropyl-2-(isopropylamino)troponiminato}phenylzinc] (4): 0.10 g of {ATI(iPr)$_2$}H (0.5 mmol) in 5 mL of toluene; 0.13 g of ZnPh$_2$ (0.6 mmol) in 5 mL of toluene; yield 0.06 g (37%). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ = 1.15 (d, J = 6.2 Hz, 12 H), 3.77 (sept, J = 5.5 Hz, 2 H), 6.39 (t, J = 9.1 Hz, 1 H), 6.63 (d, J = 11.6 Hz, 2 H), 6.98 (t, J = 9.2 Hz, 2 H), 7.30 (t, J = 7.4 Hz, 1 H), 7.41 (t, J = 7.1 Hz, 2 H), 7.84 (d, J = 6.5 Hz, 2 H) ppm. ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ = 24.7, 48.4, 112.3, 118.3, 127.0, 128.5, 134.7, 138.9, 152.2, 160.2 ppm. MS (EI, 80 eV): *m*/*z* (%) = 344 (100) [M$^+$], 333 (31), 332 (15), 331 (46), 330 (17), 329 (77), 204 (10), 189 (10), 187 (37), 173 (21), 144 (26), 131 (16), 78 (81), 77 (23). HRMS: C$_{19}$H$_{24}$N$_2$Zn: calcd. 344.12311; found: 344.12245.

[{*N*-Isopropyl-2-(isopropylamino)-5-(phenylsulfanyl)troponiminato}phenylzinc] (5): 0.16 g of {PhS-ATI(iPr)$_2$}H (0.5 mmol) in 10 mL of toluene, 0.10 g of ZnPh$_2$ (0.5 mmol) in 10 mL of toluene; yield 0.08 g (37%). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ = 0.94 (d, J = 6.2 Hz, 12 H), 3.47 (sept, J = 6.2 Hz, 2 H), 6.23 (d, J = 11.9 Hz, 2 H), 6.74 (t, J = 7.3 Hz, 1 H), 6.88 (t, J = 7.5 Hz, 2 H), 7.00 (d, J = 1.6 Hz, 1 H), 7.16 (m, 2 H), 7.25 (m, 4 H), 7.66 (dd, J = 7.7, J = 1.3 Hz, 2 H) ppm. ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ = 24.5, 48.6, 111.5, 120.2, 125.6, 127.1, 127.7, 128.5, 129.3, 138.8, 141.1, 141.5, 151.5, 160.0 ppm. MS (EI, 80 eV): *m*/*z* (%) = 452 (100) [M$^+$], 437 (22), 422 (21), 409 (10), 269 (24). C$_{25}$H$_{28}$N$_2$SZn (453.95): calcd. C 66.15, H 6.22, N 6.17; found C 65.15, H 6.40, N 5.81. HRMS: C$_{25}$H$_{28}$N$_2$SZn calcd. 452.12646; found: 452.12559.

[{*N*-Cyclohexyl-2-(cyclohexylamino)troponiminato}phenylzinc] (6): 0.18 g of ZnPh$_2$ (0.8 mmol); 0.23 g {ATI(Cy)$_2$}H (0.8 mmol) in 15 mL of toluene; yield 0.30 g (87%). ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ = 1.00 (m, 2 H), 1.17 (m, 4 H), 1.44 (m, 4 H), 1.55 (m, 6 H), 1.88 (m, 4 H), 3.56 (tt, J = 3.9, J = 10.0 Hz, 2 H), 6.41 (t, J = 9.2 Hz, 1 H), 6.81 (d, J = 11.4 Hz, 2 H), 7.00 (m, 2 H), 7.30 (m, 1 H), 7.44 (t, J = 7.7 Hz, 2 H), 7.92 (m, 2 H) ppm. ^{13}C NMR (C$_6$D$_6$,

100 MHz): δ = 25.9, 26.0, 35.5, 57.4, 112.3, 118.4, 127.0, 128.4, 134.6, 139.0, 152.2, 160.3 ppm. MS (EI, 80 eV): *m*/*z* (%) = 424 (100) [M$^+$], 381 (30), 346 (16), 283 (18), 213 (51). $C_{25}H_{32}N_2Zn$ (423.92): calcd. C 70.50, H 7.57, N 6.58; found C 70.16, H 6.99, N 6.45.

General Procedure for the Synthesis of [{R^1-ATI(R^2)$_2$}Zn{NSiMe$_3$}$_2$] 7–9: A solution of the aminotroponimine in of toluene was slowly added to a solution of [Zn{N(SiMe$_3$)$_2$}$_2$] in toluene at 0 °C. The combined solution was slowly warmed to room temperature and stirred for 5 h. The solution was filtered and all volatiles were removed under reduced pressure. Then, the yellow residue was washed twice with *n*-pentane (5 mL).

[{*N*-Isopropyl-2-(isopropylamino)troponiminato}bis(trimethylsilyl)-amidozinc] (7): 3.78 g of [Zn{N(SiMe$_3$)$_2$}$_2$] (9.8 mmol) in 50 mL of toluene; 2.00 g of {ATI(*i*Pr)$_2$}H (9.8 mmol) in 50 mL of toluene. Crystals suitable for single X-ray diffraction were obtained from toluene at –40 °C; yield 2.62 g (62%). ^{1}H NMR (C_6D_6, 400 MHz): δ = 0.22 (s, 18 H), 1.27 (d, *J* = 6.2 Hz, 12 H), 3.76 (sept, *J* = 5.8 Hz, 2 H), 6.34 (t, *J* = 10.4 Hz, 1 H), 6.53 (d, *J* = 11.5 Hz, 2 H), 6.90 (t, *J* = 9.3 Hz, 2 H) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 5.2, 24.4, 48.7, 112.7, 118.7, 134.9, 159.5 ppm. MS (EI, 80 eV): *m*/*z* (%) = 427 (42) [M$^+$], 416 (11), 204 (43), 161 (37), 144 (44), 131 (22). $C_{19}H_{37}N_3Si_2Zn$ (429.07): calcd. C 53.18, H 8.69, N 9.79; found C 53.09, H 8.68, N 9.39.

[{*N*-Isopropyl-2-(isopropylamino)-5-(phenylsulfanyl)troponiminato}-bis(trimethylsilyl)amidozinc] (8): 0.14 g of [Zn{N(SiMe$_3$)$_2$}$_2$] (0.4 mmol) in 10 mL of toluene; 0.10 g of {PhS-ATI(*i*Pr)$_2$}H (0.3 mmol) in 10 mL of toluene. Crystals suitable for single X-ray diffraction were obtained from toluene at –20 °C; yield 0.10 g (56%). ^{1}H NMR (C_6D_6, 400 MHz): δ = 0.28 (s, 18 H), 1.21 (d, *J* = 6.4 Hz, 12 H), 3.63 (sept, *J* = 6.3 Hz, 2 H), 6.33 (d, *J* = 12.8 Hz, 2 H), 6.90 (m, 1 H), 7.01 (m, 2 H), 7.31 (m, 2 H), 7.36 (m, 1 H), 7.39 (m, 1 H) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 5.6, 24.6, 48.9, 111.9, 121.2, 125.7, 128.2, 129.3, 140.8, 141.6, 159.3 ppm. MS (EI, 80 eV): *m*/*z* (%) = 535 (83) [M$^+$], 520 (19), 390 (11), 145 (100). HRMS: $C_{25}H_{41}N_3SSi_2Zn$ calcd. 535.18512; found 535.18397.

[{*N*-Cyclohexyl-2-(cyclohexylamino)troponiminato}bis(trimethylsilyl)amidozinc] (9): 0.25 mL of [Zn{NSiMe$_3$}$_2$}$_2$] (0.7 mmol) in 10 mL of toluene; 0.21 g of {ATI(Cy)$_2$}H (0.7 mmol) in 10 mL of toluene. Crystals suitable for single X-ray diffraction were obtained from toluene at –20 °C; yield 0.28 g (74%). ^{1}H NMR (C_6D_6, 400 MHz): δ = 0.37 (s, 18 H), 1.24 (m, 8 H), 1.74 (m, 8 H), 1.97 (m, 4 H), 3.56 (m, 2 H), 6.37 (t, *J* = 9.2 Hz, 1 H), 6.74 (d, *J* = 11.5 Hz, 2 H), 6.93 (t, *J* = 11.5 Hz, 2 H) ppm. ^{13}C NMR (C_6D_6, 100 MHz): δ = 5.8, 25.8, 26.3, 35.2, 57.4, 112.7, 118.8, 134.8, 159.5. $C_{25}H_{45}N_3Si_2Zn$ (509.20): calcd. C 58.97, H 8.91, N 8.25; found C 58.66, H 8.93, N 8.00 ppm.

X-ray Crystallographic Studies of 4–8: A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the –70 °C cold stream of STOE IPDS 2T diffractometer. The calculations given below were carried out with a personal computer (processor: Intel Pentium® Core2Duo).

Crystal Structure for 4: $C_{19}H_{24}N_2Zn$, *M* = 345.77, monoclinic, *a* = 10.22(2) Å, *b* = 17.543(2) Å, *c* = 10.7487(12) Å, β = 117.669(10)°, *V* = 1705.8(4) Å^3, *T* = 200 K, space group $P2_1/c$ (No. 14), *Z* = 4, μ(Mo-K_α) = 1.438 mm^{-1}, 8825 reflections measured, 2998 reflections unique (R_{int} = 0.0330), observed data [$I > 2\sigma(I)$] = 2552, R_1 = 0.0345, wR_2 = 0.0883. The structure was solved and refined using SHELXS-97[21] and SHELXL-97.[20]

Crystal Structure for 5: $C_{25}H_{28}N_2SZn$, *M* = 453.92, monoclinic, *a* = 7.8224(6) Å, *b* = 25.198(2) Å, *c* = 11.2083(8) Å, β = 92.922(6)°, *V* = 2206.3(3) Å^3, *T* = 200 K, space group $P2_1/c$ (No. 14), *Z* = 4, μ(Mo-K_α) = 1.221 mm^{-1}, 11586 reflections measured, 3895 reflections unique (R_{int} = 0.0818), observed data [$I > 2\sigma(I)$] = 3049, R_1 = 0.0401, wR_2 = 0.0997. The structure was solved and refined using SHELXS-97[20] and SHELXL-97.[20]

Crystal Structure for 6: $C_{25}H_{32}N_2Zn$, *M* = 425.90, monoclinic, *a* = 5.8093(3) Å, *b* = 15.8097(11) Å, *c* = 11.5409(10) Å, β = 92.039(7)°, *V* = 1059.28(15) Å^3, *T* = 200 K, space group $P2_1$ (No. 4), *Z* = 2, μ(Mo-K_α) = 1.172 mm^{-1}, 5034 reflections measured, 3360 reflections unique (R_{int} = 0.0269), observed data [$I > 2\sigma(I)$] = 3144, R_1 = 0.0261, wR_2 = 0.0659. Flack parameter 0.038(11). The structure was solved and refined using SHELXS-97[20] and SHELXL-97.[20]

Crystal Structure 7: $C_{19}H_{37}N_3Si_2Zn$, *M* = 429.07, monoclinic, *a* = 11.1384(8) Å, *b* = 22.413(2) Å, *c* = 9.7801(7) Å, β = 99.387(6)°, *V* = 2408.8(3) Å^3, *T* = 200 K, space group $P2_1/c$ (No. 14), *Z* = 4, μ(Mo-K_a) = 1.126 mm^{-1}, 16683 reflections measured, 4250 reflections unique (R_{int} = 0.0750), observed data [$I > 2\sigma(I)$] = 3347, R_1 = 0.0963, wR_2 = 0.2725. The structure was solved and refined using SHELXS-97[20] and SHELXL-97.[20]

Crystal Structure for 8: $C_{25}H_{41}N_3SSiZn$ + 1/2 C_7H_8 (toluene), *M* = 583.29, monoclinic, *a* = 19.1619(15) Å, *b* = 13.2431(6) Å, *c* = 12.9104(12) Å, β = 103.455(7)°, *V* = 3186.3(4) Å^3, *T* = 200 K, space group $P2_1/c$ (No. 14), *Z* = 4, μ(Mo-K_a) = 0.932 mm^{-1}, 14316 reflections measured, 5508 reflections unique (R_{int} = 0.0575), observed data [$I > 2\sigma(I)$] = 3887, R_1 = 0.0474, wR_2 = 0.1133. The structure was solved and refined using SHELXS-97[20] and SHELXL-97.[20]

CCDC-686890 (for **4**), -686891 (for **5**), -686892 (for **6**), -686893 (for **7**), -686894 (for **8**) 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.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie. J.-S. Herrmann is acknowledged for growing single-crystals of compound **4**.

[1] R. H. Prince, *Adv. Inorg. Chem. Radiochem.* **1979**, *22*, 349–440.
[2] E. Frankland, *Justus Liebigs Ann. Chem.* **1849**, *71*, 171–213.
[3] The Nobel Foundation, *Nobel Lectures Chemistry 1901–1921 and 1922–1941*, Elsevier Publishing Company, Amsterdam, London, New York, **1966**, vol. *1901–1921*; see also: http://nobelprize.org/nobel_prizes/chemistry/laureates/1912/grignard-lecture.pdf.
[4] N. N. Greenwood, A. Earnshaw *Chemistry of the Elements*, Pergamon Press, Oxford, **1984**.
[5] E. Nakamura, in *Organometallics in Synthesis – A Manual* (Ed.: M. Schlosser), Wiley, Chichester, **2002**, p. 579–664.
[6] P. Knochel, R. D. Singer, *Chem. Rev.* **1993**, *93*, 2117–2188.
[7] B. Cornils, in: *Catalysis from A-Z* (Eds.: B. Cornils, W. A. Herrmann, R. Schlögel, C.-H. Wong), Wiley-VCH, Weinheim, **2003**, p. 838–839.
[8] For recent reviews see: a) T. E. Müller, K. C. Hultzsch, M. Yus, F. Foubelo, M. Tada, *Chem. Rev.* **2008**, *108*, 3795–3892; b) R. A. Widenhoefer, X. Han, *Eur. J. Org. Chem.* **2006**, 4555–4563; c) K. C. Hultzsch, *Adv. Synth. Catal.* **2005**, *347*, 367–391; d) S. Hong, T. J. Marks, *Acc. Chem. Res.* **2004**, *37*, 673–686; e) I. Bytschkov, S. Doye, *Eur. J. Org. Chem.* **2003**, 935–946; f) F. Pohlki, S. Doye, *Chem. Soc. Rev.* **2003**, *32*, 104–114; g) T. E. Müller in J. T. Horváth, *Encyclopedia of Catalysis*, John Wiley & Sons, New York, **2002**; h) J. Seayad, A. Tillack, C. G. Hartung, M. Beller, *Adv. Synth. Catal.* **2002**, *344*, 795–813; i)

J.-J. Brunet, D. Neibecker in *Catalytic Heterofunctionalizations* (Eds.: A. Togni, H. Grützmacher), VCH, Weinheim, **2001**; j) T. E. Müller, M. Beller, *Chem. Rev.* **1998**, *98*, 675–703.

[9] a) D. Riegert, J. Collin, A. Meddour, E. Schulz, A. Trifonov, *J. Org. Chem.* **2006**, *71*, 2514–2517; b) D. V. Gribkov, K. C. Hultzsch, F. Hampel, *J. Am. Chem. Soc.* **2006**, *128*, 3748–3759.

[10] a) M. C. Wood, D. C. Leitch, C. S. Yeung, J. A. Kozak, L. L. Schafer, *Angew. Chem. Int. Ed.* **2007**, *46*, 354–358; b) L. T. Kasper, B. Fingerhut, L. Ackermann, *Angew. Chem. Int. Ed.* **2005**, *44*, 5972–5974; c) A. Heutling, F. Pohlki, I. Bytschkov, S. Doye, *Angew. Chem. Int. Ed.* **2005**, *44*, 2951–2954.

[11] a) J. L. McBee, A. T. Bell, T. D. Tilley, *J. Am. Chem. Soc.* **2008**, *130*, 16562–16571; b) S. L. Dabb, B. Messerle, *Dalton Trans.* **2008**, 6368–6371; c) J. Zhou, J. F. Hartwig, *J. Am. Chem. Soc.* **2008**, *130*, 12220–12221; d) A. Takemiya, J. F. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 6042–6043; e) F. E. Michael, B. M. Cochran, *J. Am. Chem. Soc.* **2006**, *128*, 4246–4247; f) G. B. Bajracharya, Z. Huo, Y. Yamamoto, *J. Org. Chem.* **2005**, *70*, 4883–4886; g) C. F. Bender, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2005**, *127*, 1070–1071.

[12] a) M. R. Crimmin, I. J. Caseley, M. S. Hill, *J. Am. Chem. Soc.* **2005**, *127*, 2042–2043; b) S. Datta, P. W. Roesky, S. Blechert, *Organometallics* **2007**, *26*, 4392–4394.

[13] a) X. Han, R. A. Widenhoefer, *Angew. Chem.* **2006**, *118*, 1779–1781; *Angew. Chem. Int. Ed.* **2006**, *45*, 1747–1749; b) C. Brouwer, C. He, *Angew. Chem.* **2006**, *118*, 1744–1747; *Angew. Chem. Int. Ed.* **2006**, *45*, 1776–1779; c) J.-E. Kang, H.-B. Kim, J.-W. Lee, S. Shin, *Org. Lett.* **2006**, *8*, 3537–3540.

[14] 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.

[15] 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.

[16] M. Dochnahl, K. Löhnwitz, J.-W. Pissarek, P. W. Roesky, S. Blechert, *Dalton Trans.* **2008**, 2844–2848.

[17] S. Cai, D. M. Hoffmann, D. A. Wiedra, *Organometallics* **1996**, *15*, 1023–1032.

[18] D.-Y. Lee, J. F. Hartwig, *Org. Lett.* **2005**, *7*, 1169–1172.

[19] K. Gräbe, F. Pohlki, S. Doye, *Eur. J. Org. Chem.* **2008**, 4815–4823.

[20] H. V. R. Dias, W. Jin, R. E. Ratcliff, *Inorg. Chem.* **1995**, *34*, 6100–6105.

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

Received: September 9, 2008
Published Online: February 19, 2009

