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# Intramolecular Hydroamination with Homogeneous Zinc Catalysts: Evaluation of Substituent Effects in *N*,*N*′-Disubstituted Aminotroponiminate Zinc Complexes

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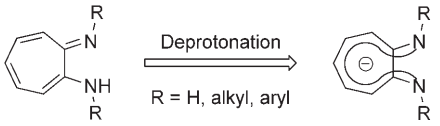
**Abstract:** A series of symmetrical and unsymmetrical *N*,*N*′-disubstituted aminotroponimines (ATIHs) have been prepared. Substituents ranging from linear to cyclic alkyl groups, chelating ethers, and aryl groups were employed. The corresponding aminotroponiminate zinc complexes were then synthesized and characterized by a number of techniques, including by X-ray crystallography. Herein we report on the investigations into their activity in the intramolecular hydroamination of nonactivated alkenes. We also demonstrate that complexes bearing ligands with cyclic alkyl groups show superior activity in a number of selected reactions with functionalized aminoalkenes.

**Keywords:** heterocycles · homogeneous catalysis · hydroamination · substituent effects · zinc

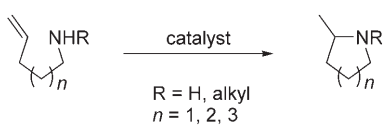
## Introduction

Aminotroponimines (ATIHs) are a well-known class of ligands that were discovered in 1960s.[1] Early studies demonstrated that these interesting molecules display a very rich coordination chemistry. Thus a large number of main-group and transition-metal complexes have been synthesized.[2] ATI ligands behave as anionic bidentate nitrogen donors and form very stable chelate complexes. Although the imine and amine C–N bonds in the neutral ATIH ligand have different bond lengths, the anionic ligand usually shows perfect $C_2$ symmetry, indicating a delocalization of the negative charge through the seven-membered ring (Scheme 1).[3]




Scheme 1. Aminotroponiminates as anionic bidentate ligands.

The synthesis of nitrogen-containing molecules is of great interest for academic and industrial researchers as a large number of natural products and pharmaceuticals contain amine or amide moieties.[4] Currently, these compounds are prepared in multistep reactions leading to substantial numbers of byproducts and waste. Thus, hydroamination, the direct addition of an N–H bond to a C–C multiple bond is potentially an economically and environmentally superior process (Scheme 2).[5] A number of catalysts have been used in this reaction based mainly on lithium,[6] Group 4 metals,[7] the lanthanides,[8–10] the platinum metals,[11] and more recently on calcium,[12] copper,[13] silver,[14] and gold.[15] Early transition metals offer the advantage of being highly effective




Scheme 2. Intramolecular hydroamination of alkenes.

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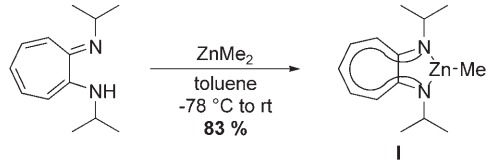
for this transformation, however, their sensitivity towards air and moisture and their incompatibility with polar functional groups limit their use in organic synthesis. In general, late transition metals are relatively stable and compatible with a large number of functional groups. On the other hand, they are rather expensive and some of them are also toxic.

Recently, we reported on the zinc-catalyzed hydroamination of unactivated alkynes and olefins.[16,17] We were able to demonstrate that the new catalyst *N*-isopropyl-*N*′-(isopropylamino)troponiminato(methyl)zinc, [{(*i*Pr)$_2$ATI}ZnMe] (**I**), readily reacts with a large number of functionalized aminoolefins and aminoalkynes leading to five-, six-, and seven-membered heterocycles. Zinc complex **I** has several advantages over the previously known catalysts: It is easily prepared in high yields (Scheme 3), it shows an unprecedented tolerance towards polar functional groups, and it is relatively stable towards air and moisture. In comparison with other late-transition-metal catalysts it shows high reactivity and furthermore zinc is an inexpensive and nontoxic metal which makes its use in catalysis attractive.[16a]

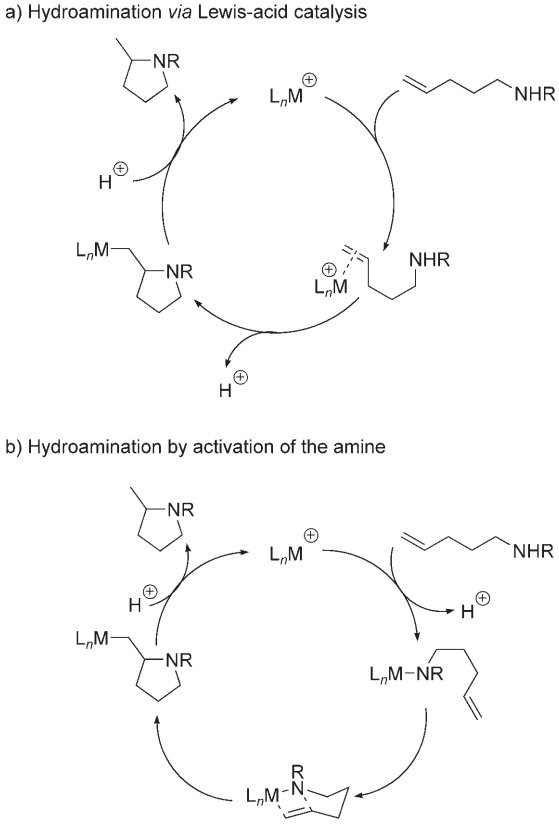



Scheme 3. Synthesis and structure of [{(*i*Pr)$_2$ATI}ZnMe] (**I**).

In principle, zinc-catalyzed hydroamination can proceed through two mechanistic pathways: a) Lewis acid catalysis with activation of the C–C double (or triple) bond or b) activation of the amine leading to a metalloamide which then undergoes olefin insertion (Scheme 4).[5b]

It has been reported that hydroamination with lanthanides and early transition metals proceeds through the activation of the N–H bond.[5k] On the other hand, with late transition metals, activation of the C–C multiple bond with concomitant attack by the nitrogen nucleophile has been postulated.[18,19] It is still to be revealed which of the two mechanistic possibilities is applicable to the case of zinc-catalyzed hydroamination.

To find more active and stable catalysts for catalytic hydroamination, we focussed our attention on the modification of the ligand structure. We postulated that modifications of the alkyl groups on the nitrogen atoms should have a major effect as they may influence the coordination sphere of the zinc atom, that is, the number of molecules that are bound to the zinc atom. Modifications to the alkyl groups may also facilitate ring closure and in particular the displacement of product molecules from the catalyst by substrate molecules as a result of steric effects. The introduction of large alkyl or hemilabile coordinating groups could also protect the active site of the catalyst from bimolecular decomposition.



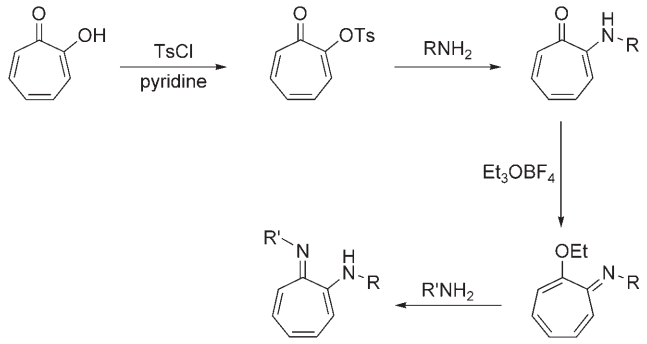

Scheme 4. Possible reaction mechanisms for the transition-metal-catalyzed hydroamination reaction.[18]

Herein, we summarize the results of our investigations on the effect of steric modifications to the nitrogen substituents, including the cyclohexyl-substituted catalyst **3c**, whose catalytic activity has already been reported.[16b]

## Results and Discussion

Based on the above-mentioned assumptions we investigated the effect of alteration of the *N*-alkyl substituents of the first generation catalyst **I**. Three different modifications were examined. 1) Steric effects, by the introduction of alkyl groups varying from small methyl to larger benzyl and cyclohexyl groups. This included the sterically demanding 1-ethylpropyl group and the cyclododecyl group. 2) Chelation, by probing the effects of tethered ethers on the behavior of zinc complexes. This entailed the study of different tether lengths, which would give oxazametallacycles with different ring sizes, and their effect on the catalyst. 3) Electronic effects, by investigating the effect of basicity, and hence the donor strength of the ligand's nitrogen atoms, with complexes bearing *N*,*N*′-diaryltroponimine ligands. These would be expected to be poorer σ donors and were compared with bis-alkyl complexes.



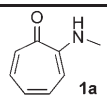
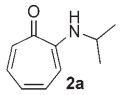
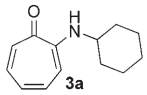
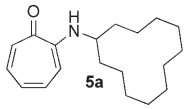
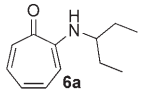
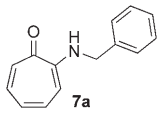
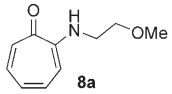
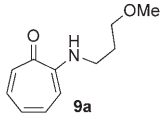
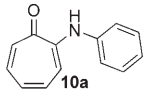

Scheme 5. Synthetic path to aminotroponimines starting from tropolone.

**Ligand synthesis**: The synthesis of aminotroponimines is a well established procedure (Scheme 5).[20] First, tropolone, which can be prepared in high yields on a multigram scale,[21] is converted into 2-tosyloxytropone.[22,23] The latter is then treated with the corresponding amine to give the substituted 2-aminotropone. Activation with Meerwein's salt ($Et_3OBF_4$) followed by aminolysis of the resulting vinylogous ether gives the desired aminotroponimine. This stepwise approach to aminotroponimines has the advantage of also enabling the synthesis of unsymmetrical derivatives.

To obtain high yields reproducibly, the procedures used for the synthesis of 2-aminotropones and aminotroponimines were modified. For amines with low boiling points, a large excess of the amine was used (General procedure A). The reactions were then conducted in a neat solution of 2-tosyloxytropolone and the amine. On the other hand, for reactions with more expensive and less volatile or even solid amines we had to find a stoichiometric procedure. In these cases reactions were performed in refluxing ethanol using triethylamine as a base (General Procedure B). The results of the reactions are summarized in Table 1. The yields for the synthesis of 2-aminotropones are in the range of 70–94%. The best results were obtained when a large excess of the corresponding amine was used. 2-Methylaminotropone (**1a**) was synthesized in 70% yield when 2-tosyloxytropone was treated with a 40% aqueous solution of methylamine.[24] The already known 2-(isopropylamino)tropone (**2a**) was obtained in high yield by modification of a literature procedure.[20] 2-(Cyclohexylamino)tropone (**3a**) was synthesized in a very high yield of 92%. 2-(Cyclododecylamino)- (**5a**) and 2-(1-ethylpropylamino)tropone (**6a**) were prepared by applying the stoichiometric procedure B. Reaction with benzylamine afforded 2-benzylaminotropone (**7a**) in a reasonable yield of 73%. Aminotropones **8a** and **9a** bearing ether moieties were also obtained in excellent yields of 94 and 92%, respectively (Table 1, entries 7 and 8). The 94% yield obtained for the synthesis of 2-(phenylamino)tropone (**10a**) is higher than the yield reported in the literature.[3]

Having prepared this series of substituted 2-aminotropones we started to synthesize the corresponding aminotroponimines (Table 2). Two procedures were used in the final step of the ATI ligand synthesis. As for the earlier step, the use of a large excess of the amine was suitable for cheap, volatile amines (General procedure C), whereas 2 equivalents of the more expensive, nonvolatile amines were used in reactions with activated aminotropone derivatives in ethanol in the presence of triethylamine as an external base (General procedure D).

Table 1. Synthesis of substituted 2-aminotropones.[a]

| Entry | Amine | Product | General procedure | Yield [%][b] |
|---|---|---|---|---|
| 1 | $MeNH_2$ |  **1a** | A | 70 |
| 2 | $iPrNH_2$ |  **2a** | A | 89 |
| 3 | $CyNH_2$ |  **3a** | A | 92 |
| 4 | $C_{12}H_{23}NH_2$ |  **5a** | B | 74 |
| 5 | $C_5H_{11}NH_2$ |  **6a** | B | 92 |
| 6 | $BnNH_2$ |  **7a** | A | 73 |
| 7 | $MeO(CH_2)_2NH_2$ |  **8a** | A | 94 |
| 8 | $MeO(CH_2)_3NH_2$ |  **9a** | A | 92 |
| 9 | $PhNH_2$ |  **10a** | B | 94 |

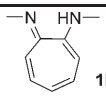
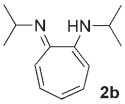
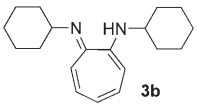
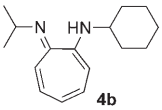
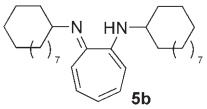
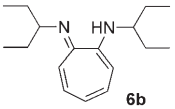
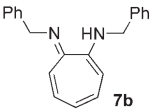
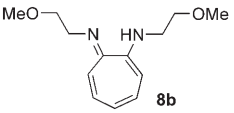
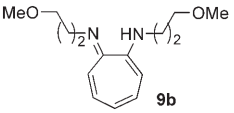
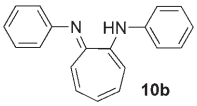
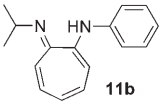
[a] General procedure A: 2-Tosyloxytropone, amine (excess), 0°C to room temperature, 16 h. General procedure B: 2-Tosyloxytropone (1 equiv), amine (1.2 equiv), $NEt_3$ (1.5 equiv), EtOH, reflux, 6 h. [b] Isolated yield of >95% purity.

By using these procedures, the corresponding aminotroponimines were synthesized in high yields. The only exceptions were *N*-methyl-2-(methylamino)troponimine[24] [$(Me)_2$ATI]H (**1b**), which was synthesized in a moderate yield of 50%, and *N*-phenyl-2-(phenylamino)troponimine[3] [$(Ph)_2$ATI]H (**10b**). The latter was isolated in a yield of only 35% which is in agreement with the literature and is attributed to the poor nucleophilicity of aniline.

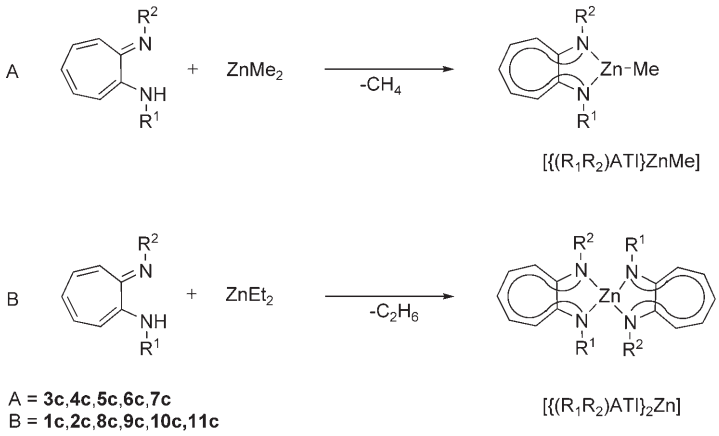
**Metal complex syntheses**: The previously reported complex [{$(iPr)_2$ATI}ZnMe] (**I**) was prepared by reaction of [$(iPr)_2$ATI]H with $ZnMe_2$ in high yield.[16a] In a similar synthetic procedure we treated the neutral aminotroponimines

Table 2. Synthesis of *N*,*N*′-disubstituted aminotroponimines.[a]

| Entry | 2-Aminotropone | Product | General procedure | Yield [%][b] |
|---|---|---|---|---|
| 1 | **1a** |  **1b** | C | 50 |
| 2 | **2a** |  **2b** | C | 83 |
| 3 | **3a** |  **3b** | C | 90 |
| 4 | **3a** |  **4b** | C | 72 |
| 5 | **5a** |  **5b** | D | 74 |
| 6 | **6a** |  **6b** | D | 88 |
| 7 | **7a** |  **7b** | D | 74 |
| 8 | **8a** |  **8b** | C | 59 |
| 9 | **9a** |  **9b** | C | 83 |
| 10 | **10a** |  **10b** | D | 35 |
| 11 | **10a** |  **11b** | C | 80 |

[a] General procedure C: Aminotropone (1 equiv), $Et_3OBF_4$ (1 equiv), $CH_2Cl_2$, room temperature, 3 h, then amine (excess) overnight. General procedure D: Aminotropone (1 equiv), $Et_3OBF_4$ (1 equiv), $CH_2Cl_2$, room temperature, 3 h, then amine (2 equiv), ethanol, room temperature. [b] Isolated yield of >95% purity.




Scheme 6. Synthesis of aminotroponiminate-zinc complexes.

[(R/R′)ATI]H (**1b** and **3–11b**) with $ZnMe_2$ in toluene at room temperature (Scheme 6, Table 3).

All reactions were judged to be complete after the evolution of gas had stopped which was usually the case after three hours. Under these conditions the reaction of ligands **3b–7b** led exclusively to the formation of high yields of methylzinc complexes of the general composition [{(R/R′)ATI}ZnMe] (**3c–7c**) in (Scheme 6A). In contrast, by using ligands **1b** and **8b–11b**, homoleptic complexes of composition [{(R/R′)ATI}$_2$Zn] (**1c** and **8c–11c**) were obtained (Scheme 6B). The yields of the latter complexes and compound **2c** were then optimized by using the appropriate stoichiometric ratio of the ligand and $ZnEt_2$. Complex **8c** was synthesized in THF because of the low solubility of ligand **8b** in toluene. Clearly steric arguments are not the major factors controlling complex formation. We suggest that instead the p$K_a$ of the aminotroponimines is one factor that influences the reactivity. We and others have previously observed that the reactivity of the methyl group in compounds of general composition L-ZnMe (L = ligand) is less than in $ZnMe_2$.[16,25] Thus, substitution of the second methyl group is eased by using more acidic ligands. Clearly the phenyl-substituted ligands **10b** and **11b** are such species. Moreover, ancillary groups on the aminotroponimines also influence the reactivity, as observed in **8b** and **9b**. We suggest that the oxygen atoms of the tethers of the first ligand in an [{(R)$_2$ATI}ZnMe] intermediate coordinate to the zinc atom and thus increase the reactivity of the remaining methyl group. Nevertheless, by using appropriate ligands both mono- and disubstituted complexes can be obtained. We observed this previously with the *n*-propyl-bridged bis-aminotroponimine H$_2$[(*i*Pr)TP].[26] In a similar way [(*i*Pr)$_2$ATI]H (**2b**) can react to give either [{(*i*Pr)$_2$ATI}ZnMe] (**I**) or [{(*i*Pr)$_2$ATI}$_2$Zn] (**2c**).

These new complexes were characterized by standard analytical/spectroscopic techniques and the solid-state structures of selected compounds were established by single-crystal X-ray diffraction. A comparison of the $^1$H and $^{13}$C{$^1$H} NMR spectra of the starting material $ZnMe_2$ ($^1$H: $\delta$ = 0.51 ppm, $^{13}$C{$^1$H} $\delta$ = −4.2 ppm)[27] with those of the complexes **3c** ($^1$H: $\delta$ = 0.08 ppm, $^{13}$C{$^1$H} $\delta$ = −9.9 ppm), **4c** ($^1$H: $\delta$ = 0.04 ppm, $^{13}$C{$^1$H} $\delta$ = −9.9 ppm), **5c** ($^1$H: $\delta$ = 0.13 ppm, $^{13}$C{$^1$H} $\delta$ = −10.1 ppm), **6c** ($^1$H: $\delta$ = 0.00 ppm, $^{13}$C{$^1$H} $\delta$ = −10.8 ppm), and **7c** ($^1$H: $\delta$ = −1.08 ppm, $^{13}$C{$^1$H} $\delta$ = −14.1 ppm) showed that the $^1$H and $^{13}$C{$^1$H} NMR signals of the Zn-CH$_3$ group have shifted to a higher field in each case. As observed earlier the NMR signals of the aminotroponiminate ligands are only slightly influenced by coordination. The most significant shifts are observed for those

Table 3. Synthesis of ATI-Zn complexes.[a]

| Entry | Aminotroponimine | Zinc catalyst | General procedure | Yield [%] |
|---|---|---|---|---|
| 1 | **1b** | [{(Me)$_2$ATI}$_2$Zn] (**1c**) | E/F | 61 |
| 2 | **2b** | [{(*i*Pr)$_2$ATI}$_2$Zn] (**2c**) | F | 97 |
| 3 | **3b** | [{(Cy)$_2$ATI}ZnMe] (**3c**) | E | 88 |
| 4 | **4b** | [{(Cy/*i*Pr)}ZnMe] (**4c**) | E | 47 |
| 5 | **5b** | [{(*cy*Dod)$_2$ATI}ZnMe] (**5c**) | E | 84 |
| 6 | **6b** | [{(*i*Pent)$_2$ATI}ZnMe] (**6c**) | E | 97 |
| 7 | **7b** | [{(Bn)$_2$ATI}ZnMe] (**7c**) | E[b] | 88 |
| 8 | **8b** | [{(C$_2$OMe)$_2$ATI}$_2$Zn] (**8c**) | F[c] | 85 |
| 9 | **9b** | [{(C$_3$OMe)$_2$ATI}$_2$Zn] (**9c**) | E/F | 75 |
| 10 | **10b** | [{(Ph)$_2$ATI}$_2$Zn] (**10c**) | E/F | 97 |
| 11 | **11b** | [{(Ph/*i*Pr)ATI}$_2$Zn] (**11c**) | E/F | 55 |

[a] General procedure E: Aminotroponimine (1.1 mmol), $ZnMe_2$ (1.2 mmol), room temperature, toluene, 3 h. General procedure F: aminotroponimine (1.1 mmol), $ZnEt_2$ (0.6 mmol), room temperature, toluene, 3 h. [b] Slightly modified procedure. [c] Reaction in THF.

groups that are located close to the coordinating nitrogen atoms.

**Molecular structures of 3c, 5c, and 7c in the solid state**: The structures of selected mono-, [{(R/R′)ATI}ZnMe], and disubstituted complexes, [{(R/R′)ATI}$_2$Zn], were established by single-crystal X-ray diffraction. In general, the monosubstituted complexes **3c**, **5c**, and **7c** are monomeric in the solid state (Figure 1–Figure 3). The zinc atoms are trigonal planar, coordinated by the methyl group and the two nitrogen atoms (N1 and N2) of the aminotroponiminate ligand. Compound **3c** crystallizes in the triclinic space group $P\bar{1}$ having two independent molecules in the asymmetric unit (Figure 1). The observed Zn–N bond lengths (Zn1–N1 197.0(2) pm, Zn1–N2 196.6(2) pm) are in the expected range (e.g., in **I** Zn1–N1 198.0(4) pm, Zn1–N2 195.5(4) pm).[16] The bond length between the zinc and carbon atom of the methyl group (194.4(3) pm) is also in the same region as that in **I** (194.1(5) pm). The N2-Zn1-C20 angle (137.12(11)°) is somewhat smaller than the corresponding N1-Zn1-C20 angle (140.47(11)°), which may be a result of packing effects. The N-Zn1-N bit angle inside the aminotroponiminate moiety of the ligand is smaller than that in a symmetric triangle (N1-Zn1-N2 82.17(8)°).

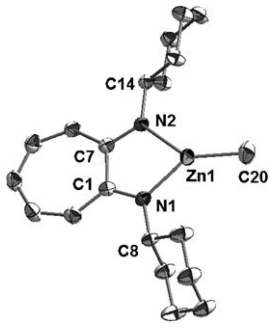



Figure 1. Perspective ORTEP view of the molecular structure of **3c**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°]: Zn1–N1 197.0(2), Zn1–N2 196.6(2), Zn1–C20 194.4(3); N1-Zn1-N2 82.17(8), Zn1-N1-C1 114.8(2), Zn1-N1-C8 123.5(2), Zn1-N2-C7 114.77(2), Zn1-N2-C14 124.5(2), N1-Zn1-C20 140.47(11), N2-Zn1-C20 137.12(11).

Crystals from compound **5c** were grown from dichloromethane at −23 °C. The solid-state structure shows that one solvent molecule is located in the unit cell. Compound **5c** crystallizes in the triclinic space group $P\bar{1}$ (Figure 2). The observed Zn–N and Zn–C bond lengths (Zn–N1 197.1(2) pm, Zn–N2 197.0(2) pm, and Zn–C32 194.1(3)) and angles are as expected. As observed for **3c** the N-Zn-C32 angles are somewhat different (N1-Zn-C32 138.53(13)° and N2-Zn-C32 (139.16(13)°).

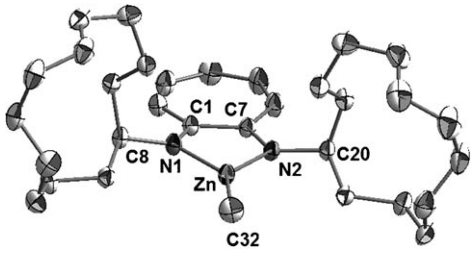



Figure 2. Perspective ORTEP view of the molecular structure of **5c**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°]: Zn–N1 197.1(2), Zn–N2 197.0(2), Zn–C32 194.2(3); N1-Zn-N2 82.31(10), Zn-N1-C1 114.30(2), Zn-N1-C8 124.56(2), Zn-N2-C7 114.68(2), Zn-N2-C20 123.46(2), N1-Zn-C32 138.53(13), N2-Zn-C32 139.16(13).

Compound **7c** crystallizes in the orthorhombic space group *Pbcn* with four molecules in the unit cell (Figure 3). A crystallographic $C_2$ axis is observed along Zn and C12. The bond lengths between the zinc and nitrogen atoms (Zn–N 197.68(2) pm) and between the zinc and methyl carbon atom (Zn–C12 194.1(3) pm) are in the same range as those in **3c**, **5c**, and **I**.

**Molecular structures of 1c, 8c, 9c, and 10c in the solid state**: The solid-state molecular structures of the disubstituted complexes **1c**, **8c**, **9c**, and **10c** were also determined by single-crystal X-ray diffraction. In all these compounds the zinc atom is surrounded by two aminotroponiminate ligands. Thus, the zinc atoms are tetracoordinated by four nitrogen atoms forming distorted tetrahedral coordination polyhedra (Figures 4–7). The distortion of the coordination polyhedra is a result of the fixed bite angle (N-Zn-N) of the aminotroponiminate ligand. Compound **1c** crystallizes in the orthorhombic space group *Pbcn* having four molecules in the unit cell (Figure 4). The zinc atom is located at a center of crys-

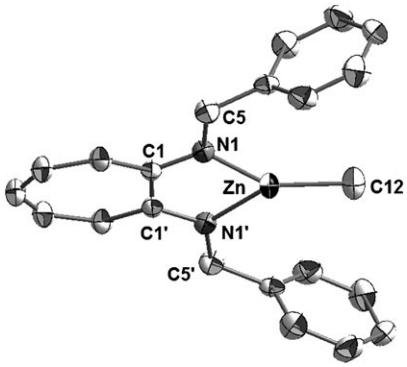



Figure 3. Perspective ORTEP view of the molecular structure of **7c**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°]: Zn–N 197.74(14), Zn–C12 194.2(3); N-Zn-N′ 81.49(8), Zn-N-C5 126.15(11), N-Zn-C12 139.25(4), Zn-N-C1 114.77(11).

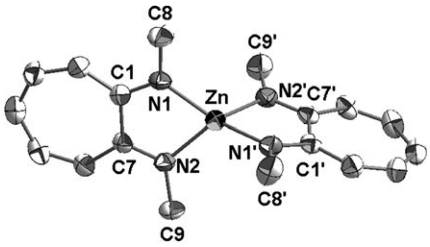



Figure 4. Perspective ORTEP view of the molecular structure of **1c**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°]: Zn–N1 198.0(3), Zn–N2 199.2(3), N1–C8 146.2(4), N2–C9 146.7(4); N1-Zn-N2 80.42(10), N1-Zn-N1′ 137.37(15), N2-Zn-N2′ 121.02(14), Zn-N1-C8 126.0(2), Zn-N1-C1 114.9(2).

tallographic symmetry, thus only one ligand is in the asymmetric unit. The bond lengths and angles are in the expected range (Zn–N1 198.0(3) pm, Zn–N2 199.2(3) pm, N1-Zn-N2 80.42(10)°, N1-Zn-N1′ 137.37(15)°, and N2-Zn-N2′ 121.02(14)°).

Compound **8c** crystallizes in the triclinic space group $P\bar{1}$ having two molecules in the unit cell (Figure 5). The oxygen atoms of the tethers do not coordinate to the zinc atom. Even though the side-chains point towards the zinc atom, the shortest Zn–O distance (Zn–O2 289.21 pm) indicates there is no interaction. We suggest that the side-chains fold as a result of packing effects.

Compound **9c** crystallizes in the tetragonal space group $I4_1/a$ having four molecules in the unit cell (Figure 6). The molecular structure shows a highly symmetrical molecule, for example, a crystallographic $C_2$ axis is observed along C4-Zn-C4′. As a result of the high symmetry all the Zn–N bonds have the same length of 198.42(11) pm. The N-Zn-N bond angles are in the expected range (N-Zn-N′ 124.83(4)°, N-Zn-N″ 81.81(6)°). As observed in compound **8c**, the oxygen atoms do not coordinate to the zinc atom in the solid state. The distance between the zinc and the oxygen atoms is over 400 pm and so no intramolecular interactions are observed.

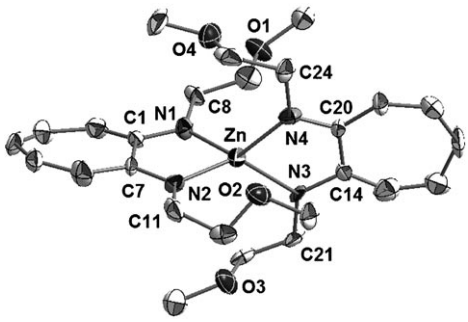



Figure 5. Perspective ORTEP view of the molecular structure of **8c**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°]: Zn–N1 201.7(2), Zn–N2 198.0(2), Zn–N4 198.5(2), Zn–N3 198.6(2), N1–C8 146.5(3), N2–C11 145.6(3), N3–C21 146.9(3), N4–C24 146.5(3); N1-Zn-N2 80.94(9), N1-Zn-N3 118.14(8), N1-Zn-N4 120.47(8), N2-Zn-N4 129.23(8), N2-Zn-N3 131.59(9), N3-Zn-N4 81.50(8).

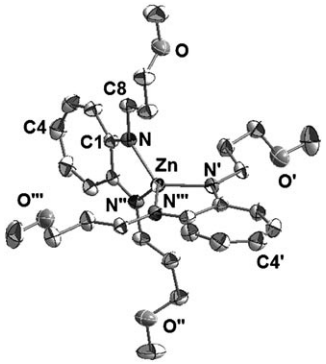



Figure 6. Perspective ORTEP view of the molecular structure of **9c**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°]: Zn–N 198.42(11); N-Zn-N′ 124.83(4), N-Zn-N″ 81.81(6), Zn-N-C1 114.39(9), Zn-N1-C8 125.62(9).

Compound **10c** crystallizes in the monoclinic space group $P2_1/c$ having four molecules in the unit cell (Figure 7). As seen for compounds **1c**, **8c**, and **9c**, the zinc atom is tetracoordinated. The phenyl rings of the aminotroponiminate ligands are rotated out of the plane of the seven-membered rings, thus breaking the symmetry of the molecule. In comparison with the previously discussed structures no significant deviations of the bond lengths and angles from the expected values were observed.

**Hydroamination reactions**: The zinc catalysts **1c**–**11c** were then tested in the catalytic hydroamination reactions of non-activated alkenes and compared with the reactions of the first generation catalyst **I**. We decided to investigate the cyclization of four different aminoalkenes **12a**–**15a**. These compounds were chosen because they possess different groups on the backbones of the carbon chains. Groups in these positions facilitate the cyclization process by the well-known Thorpe–Ingold effect.[28] On the other hand, the substrates are distinguished by different aromatic and heteroaromatic groups, providing information on the effect of heteroatoms

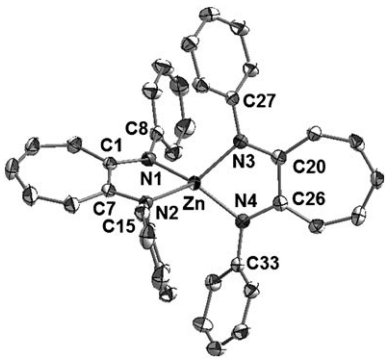


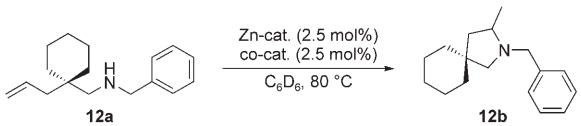

Figure 7. Perspective ORTEP view of the molecular structure of **10c**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected distances [pm] and angles [°]: Zn–N1 197.48(2), Zn–N2 198.81(2), Zn–N3 199.76(2), Zn–N4 197.08(2); N1-Zn-N2 80.80(7), N1-Zn-N3 109.67(7), N1-Zn-N4 138.73(7), N2-Zn-N3 137.51(7), N2-Zn-N4 118.86(7), N3-Zn-N4 80.93(7), Zn-N1-C1 115.59(1), Zn-N1-C8 121.25(1).

present in the molecules. All the reactions were carried out in benzene at 80 °C and a relatively low catalyst loading of 2.5 mol% was chosen. The reactions were conducted with 1 equivalent (with respect to the catalyst) of $[PhNMe_2H][B(C_5F_5)_4]$ as a co-catalyst. The cyclization of *N*-(1-allylcyclohexylmethyl)benzylamine (**12a**) was chosen as the first test substrate because this substrate is widely used in catalytic hydroamination reactions (Table 4), thus allowing the results to be compared with previously reported catalyst systems.[11]

It is apparent that there are three groups of catalyst. One group showed very high activity in the transformation carried out and comprises the first generation catalyst [{(*i*Pr)$_2$ATI}ZnMe] (**I**), [{(Cy)$_2$ATI}ZnMe] (**3c**), and [{(*cy*Dod)$_2$ATI}ZnMe] (**5c**). Use of these catalysts in the hydroamination reaction resulted in complete conversion after 1 h for **5c** and after 20–30 min for **3c** and **I**. The second group of catalysts all showed more or less the same medium activity: After 10 h, when the reaction was stopped they showed conversions of about 90%. This group consists of [{(Me)$_2$ATI}$_2$Zn] (**1c**), [{(*i*Pr)$_2$ATI}$_2$Zn] (**2c**), [{(*i*Pent)$_2$-ATI}ZnMe] (**6c**), [{(*C*$_3$OMe)$_2$ATI}$_2$Zn] (**9c**), [{(Ph)$_2$ATI}$_2$Zn] (**10c**), and [{(Ph/*i*Pr)$_2$ATI}ZnMe] (**11c**). The third group of catalysts, which are quite unreactive in this transformation, comprises [{(Bn)$_2$ATI}ZnMe] (**7c**), the unsymmetric complex [{(Cy/*i*Pr)ATI}ZnMe] (**4c**), and [{(*C*$_2$OMe)$_2$ATI}$_2$Zn] (**8c**). Catalyst **8c** was by far the least reactive giving a conversion of only 23%. From these primary experiments the following statements can be made. There is a considerable difference in reactivity between complexes bearing one or two ATI ligands (Table 4, compare entries 1 and 3). First generation catalyst **I** is much more reactive in this transformation than catalyst **2c**. There is also a large difference in reactivity between the two catalysts bearing coordinating ether groups (Table 4, entries 9 and 10). Catalyst **9c** bearing a three-carbon spacer between the nitrogen and the ether moiety proved to be much more reactive than catalyst **8c** bearing a two-carbon spacer.

We next investigated the hydroamination rates for the cyclization of *N*-(2,2-diphenylpent-4-enyl)-*N*-(furan-2-ylmethyl)amine (**13a**). Table 5 shows that in the case of aminofuran **13a** cyclohexyl-substituted catalyst **3c** again displays the highest activity. Catalyst **5c** bearing two large cyclododecyl groups was the second most active catalyst. However, it took twice as long for the reaction to reach complete conversion. First generation catalyst **I** was less active in this transformation, requiring 6 h for completion of the reaction. A larger group of catalysts needed about 7 h to reach complete conversion. For this reason it seems reasonable to postulate that in the case of substrate **13a** the coordination of the zinc atom to the substrate (or product) molecule has a major effect on the reaction rate. Catalysts **8c** and **9c** showed only minor activity in this transformation. This

Table 4. Cyclization of *N*-(1-allylcyclohexylmethyl)benzylamine (**12a**).[a]

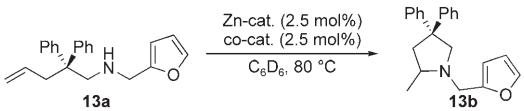



**12a** **12b**

| Entry | Catalyst | *t* [h] | Conversion[b] [%] |
|---|---|---|---|
| 1 | [{(*i*Pr)$_2$ATI}ZnMe] (**I**) | 0.5 | quant. |
| 2 | [{(Me)$_2$ATI}$_2$Zn] (**1c**) | 10 | 91 |
| 3 | [{(*i*Pr)$_2$ATI}$_2$Zn] (**2c**) | 10 | 91 |
| 4 | [{(Cy)$_2$ATI}ZnMe] (**3c**) | 0.3 | quant. (91)[c] |
| 5 | [{(Cy/*i*Pr)}ZnMe] (**4c**) | 10 | 70 |
| 6 | [{(*cy*Dod)$_2$ATI}ZnMe] (**5c**) | 1 | quant. |
| 7 | [{(*i*Pent)$_2$ATI}ZnMe] (**6c**) | 10 | 99 |
| 8 | [{(Bn)$_2$ATI}ZnMe] (**7c**) | 10 | 73 |
| 9 | [{(C$_2$OMe)$_2$ATI}$_2$Zn] (**8c**) | 10 | 23 |
| 10 | [{(C$_3$OMe)$_2$ATI}$_2$Zn] (**9c**) | 10 | 94 |
| 11 | [{(Ph)$_2$ATI}$_2$Zn] (**10c**) | 10 | 84 |
| 12 | [{(Ph/*i*Pr)ATI}$_2$Zn] (**11c**) | 10 | 88 |

[a] Reaction conditions: 2.5 mol% catalyst and 2.5 mol% $[PhNMe_2H][B(C_6F_5)_4]$ in 0.5 mL $C_6D_6$. [b] Determined by $^1$H NMR spectroscopy. [c] Isolated yield of the analytically pure sample.

Table 5. Cyclization of *N*-(2,2-diphenylpent-4-enyl)-*N*-(furan-2-ylmethyl)amine (**13a**).[a]



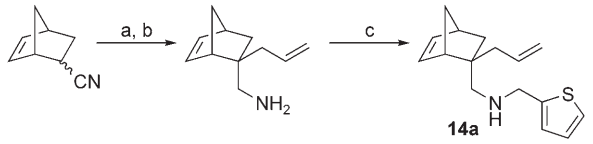

**13a** **13b**

| Entry | Catalyst | *t* [h] | Conversion[b] [%] |
|---|---|---|---|
| 1 | [{(*i*Pr)$_2$ATI}ZnMe] (**I**) | 6 | quant. |
| 2 | [{(Me)$_2$ATI}$_2$Zn] (**1c**) | 7 | 91 |
| 3 | [{(*i*Pr)$_2$ATI}$_2$Zn] (**2c**) | 12 | 91 |
| 4 | [{(Cy)$_2$ATI}ZnMe] (**3c**) | 2.5 | quant. (95)[c] |
| 5 | [{(Cy/*i*Pr)}ZnMe] (**4c**) | 7 | 96 |
| 6 | [{(*cy*Dod)$_2$ATI}ZnMe] (**5c**) | 5 | quant. |
| 7 | [{(*i*Pent)$_2$ATI}ZnMe] (**6c**) | 9 | quant. |
| 8 | [{(Bn)$_2$ATI}ZnMe] (**7c**) | 7 | quant. |
| 9 | [{(C$_2$OMe)$_2$ATI}$_2$Zn] (**8c**) | 96 | quant. |
| 10 | [{(C$_3$OMe)$_2$ATI}$_2$Zn] (**9c**) | 24 | 78 |
| 11 | [{(Ph)$_2$ATI}$_2$Zn] (**10c**) | 7 | quant. |
| 12 | [{(Ph/*i*Pr)ATI}$_2$Zn] (**11c**) | 7 | quant. |

[a] Reaction conditions: 2.5 mol% catalyst and 2.5 mol% $[PhNMe_2H][B(C_6F_5)_4]$ in 0.5 mL $C_6D_6$. [b] Determined by $^1$H NMR spectroscopy. [c] Isolated yield of the analytically pure sample.

could be explained by chelation of the ligand and the substrate to the zinc atom, making the catalyst coordinatively saturated and hence slowly reacting.

The cyclization of the norbornene derivative **14a** was investigated next (Table 6). This was prepared in three steps from norbornene-2-carbonitrile. This carbonitrile was deprotonated with LDA and alkylated with allyl bromide in excellent yield. The resulting nitrile was then treated with $LiAlH_4$ leading to the corresponding primary amine, which was treated with thiophene-2-carbaldehyde. The imine thus formed was then reduced with $NaBH_4$ to give the secondary amine **14a** (Scheme 7).




Scheme 7. Reagents and conditions: a) 1. $i$Pr$_2$NH, $n$BuLi, THF, −78 to 0 °C; 2. allyl bromide, 0 °C to RT, 94 %; b) $LiAlH_4$, $Et_2O$, 16 h, 94 %; c) 1. thiophene-2-carbaldehyde, MeOH, RT, 6 h; 2. $NaBH_4$ (1.5 equiv), 16 h, 81 %.

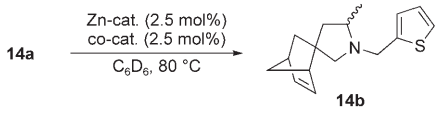
Aminoalkene **14a** is of interest because it contains both an interesting thiophene heteroaromatic system and a bicyclic system that could be further functionalized. We thought it would be interesting to compare the hydroamination conversions achieved after a certain time with the different catalysts. We estimated that the best comparison of reactivity could be made when the reaction had been in progress for several hours (Table 6).

Once again, catalyst **3c** with two cyclohexyl groups was by far the most active: It took only 2 h to reach 96 % conversion. The same conversion was obtained with catalyst **5c** after 4 h. On the other hand, the reaction with the first generation catalyst **I** was much slower and after 7 h only 88 % conversion had been achieved. This means that catalyst **I** was only as active as the majority of the investigated catalysts giving about 80–90 % yields. Astonishingly, the binary catalyst [{($i$Pr)$_2$ATI}$_2$Zn] (**2c**) reacted as fast as catalyst **I** in this transformation. This is in contrast to the cyclization of substrate **12a**, in which **I** showed a much higher activity. Again the reactions involving catalysts **8c** and **9c** bearing chelating moieties were considerably slower than the rest. Asymmetric induction by the substrate during the cyclization process was too weak to induce any diastereoselectivity in the studied reactions.

Intramolecular hydroamination of symmetrical dienes leads to the formation of heterocycles bearing a side-chain with an alkene moiety. This alkene can then be used for other synthetically interesting transformations. The reaction itself is of particular interest because during a single cyclization two new stereocenters are formed of which one is an all-carbon quaternary stereocenter. Hence it was important for us to find out if it would be possible to obtain any diastereoselectivity in this cyclization reaction. As substrate **15a** lacks large groups in the β position with respect to the amine, we had to use 5 mol % of the catalyst and 2.5 mol % of the co-catalyst in order to obtain reasonable conversions. However, all the reactions were still conducted at 80 °C (Table 7).

The cyclization of diene **15a** revealed a dramatic difference in the reactivities of the catalysts tested. Catalyst **3c** remains the most active in this reaction. Use of this catalyst in the test reaction resulted in complete conversion after only 3 h. All the other investigated catalysts were far less reactive. Catalyst **I** needed 24 h for complete conversion, that is, eight times longer, and catalyst **5c** required 60 h, the reaction thus being 20 times slower. The other catalysts were much less reactive. With the majority of the catalysts we observed only 50–70 % conversion after seven days (168 h). This means that catalyst **3c** is around 100 times more reactive than the average catalyst with this substrate. Catalysts

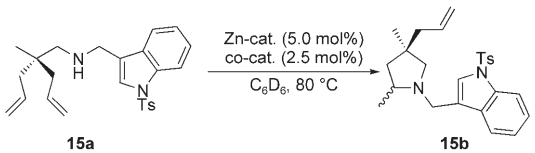
Table 6. Cyclization of bicyclic amine **14a**.[a]




| Entry | Catalyst | $t$ [h] | Conversion[b,c] [%] |
|---|---|---|---|
| 1 | [{($i$Pr)$_2$ATI}ZnMe] (**I**) | 7 | 88 |
| 2 | [{(Me)$_2$ATI}$_2$Zn] (**1c**) | 7 | 82 |
| 3 | [{($i$Pr)$_2$ATI}$_2$Zn] (**2c**) | 7 | 86 |
| 4 | [{(Cy)$_2$ATI}]ZnMe] (**3c**) | 2 | 96 (86)[d] |
| 5 | [{(Cy/$i$Pr)}]ZnMe] (**4c**) | 7 | 83 |
| 6 | [{($cy$Dod)$_2$ATI}ZnMe] (**5c**) | 4 | 96 |
| 7 | [{($i$Pent)$_2$ATI}ZnMe] (**6c**) | 7 | 91 |
| 8 | [{(Bn)$_2$ATI}ZnMe] (**7c**) | 7 | 80 |
| 9 | [{($C_2$OMe)$_2$ATI}$_2$Zn] (**8c**) | 7 | 60 |
| 10 | [{($C_3$OMe)$_2$ATI}$_2$Zn] (**9c**) | 7 | 64 |
| 11 | [{(Ph)$_2$ATI}$_2$Zn] (**10c**) | 7 | 87 |
| 12 | [{(Ph/$i$Pr)ATI}$_2$Zn] (**11c**) | 7 | 77 |

[a] Reaction conditions: 2.5 mol % catalyst and 2.5 mol % [PhNMe$_2$H][B($C_6F_5$)$_4$] in 0.5 mL $C_6D_6$. [b] Determined by $^1$H NMR spectroscopy. [c] The diastereomeric ratio (d.r.) was 1:1 in each case. [d] Isolated yield of the analytically pure sample.

Table 7. Cyclization of diene **15a**.[a]




| Entry | Catalyst | $t$ [h] | d.r. | Conversion[b] [%] |
|---|---|---|---|---|
| 1 | [($i$Pr)$_2$ATI]ZnMe (**I**) | 24 | 1.3:1 | quant. |
| 2 | [(Me)$_2$ATI]$_2$Zn (**1c**) | 168 | 1.0:1 | 62 |
| 3 | [($i$Pr)$_2$ATI]$_2$Zn (**2c**) | 168 | 1.15:1 | 56 |
| 4 | [(Cy)$_2$ATI]ZnMe (**3c**) | 3 | 1.3:1 | quant. (97)[c] |
| 5 | [(Cy/$i$Pr)ATI]ZnMe (**4c**) | 168 | 1.2:1 | 59 |
| 6 | [($cy$Dod)$_2$ATI]ZnMe (**5c**) | 60 | 1.35:1 | quant. |
| 7 | [($i$Pent)$_2$ATI]ZnMe (**6c**) | 168 | 1.2:1 | 55 |
| 8 | [(Bn)$_2$ATI]ZnMe (**7c**) | 168 | 1.3:1 | 47 |
| 9 | [($C_2$OMe)$_2$ATI]$_2$Zn (**8c**) | 168 | n.d. | 3 |
| 10 | [($C_3$OMe)$_2$ATI]$_2$Zn (**9c**) | 168 | n.d. | 25 |
| 11 | [(Ph)$_2$ATI]$_2$Zn (**10c**) | 168 | 1.1:1 | 71 |
| 12 | [(Ph/$i$Pr)ATI]$_2$Zn (**11c**) | 168 | 1.3:1 | 70 |

[a] Reaction conditions: 5.0 mol % of catalyst and 2.5 mol % of [PhNMe$_2$H][B($C_6F_5$)$_4$] in 0.5 mL $C_6D_6$. [b] Determined by $^1$H NMR spectroscopy. [c] Isolated yield of the analytically pure sample.

**8c** and **9c** were again slower than the other investigated catalysts; in particular, catalyst **8c** was virtually unreactive in this transformation. The diastereoselectivity of this transformation was very low in all the investigated cases. Catalyst **5c** bearing large cyclododecyl groups displayed the highest diastereoselectivity of 1.35:1. On the other hand, the diastereoselectivity reported for a similar compound is about the same.[10e] The observed diastereoselectivity seemed to be influenced by the size of the substituent on the ligand. When the somewhat smaller catalysts **I** and **3c** were used in the reaction, the selectivity diminished to 1.3:1. Catalyst **1c** bearing only small methyl groups showed no diastereoselectivity at all in this transformation.

## Conclusions

We have synthesized a series of aminotroponiminate zinc complexes with different substituents on the nitrogen atoms. A number of reliable procedures for the synthesis of the ligands and the catalysts have been developed. Most of the complexes could be characterized by single-crystal X-ray structure analysis. We have tested their activity in a number of hydroamination reactions. Substrates bearing several substituents on the carbon backbone and different functional groups were employed to investigate the effect of both heteroatoms and substrate geometry on the reaction. We have demonstrated that zinc catalysts are indeed highly active catalysts in this transformation. Most importantly, we discovered the new complex [{(Cy)$_2$ATI}ZnMe] (**3c**) which showed superior reactivity in all the test reactions.[16b] We attribute this to both a higher reactivity and a better long-term stability. It has also been demonstrated that alkylzinc complexes bearing one ATI ligand, [{(R/R′)ATI}ZnMe], were in general more reactive than their homoleptic counterparts, [{(R/R′)ATI}$_2$Zn]. The incorporation of donating ether groups into the ring substituents led to a loss of activity in the hydroamination reaction. We have shown that there are major differences in the reactivities of catalysts **8c** and **9c** bearing two- and three-carbon spacers, respectively, in the side-chain. It seems that coordinative saturation and thus deactivation of the catalyst is more effective with catalyst **8c**. Modification of the electronic properties by changing to phenyl groups did not have any significant effect on the reactivity. Finally, we have demonstrated that incorporation of oxygen atoms into the substrates led to prolonged reaction times. We ascribe this to the complexation of the oxophilic zinc atom which reduces its reactivity.

## Experimental Section

**General methods**: Deuteriated benzene was purchased from Deutero GmbH and stored over 4 Å molecular sieves prior to use. [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] was purchased from Strem. Silica gel 60 F$_{254}$ plates were used for TLC analyses. Flash column chromatography was performed on silica gel (MP Silica, 32–63, 60 Å). $^1$H and $^{13}$C NMR spectra were recorded with a Bruker AM 400 or DRX 500 spectrometer using $CDCl_3$ or $C_6D_6$ as solvent and the residual solvent signals were used as the internal references ($CDCl_3$: $\delta = 7.26$ and 77.0 ppm; $C_6D_6$: $\delta = 1.15$ and 128.1 ppm). The following abbreviations have been used to describe the peak patterns when appropriate: s (singlet), d (doublet), t (triplet), m (multiplet), and br (broad). Mass spectra were recorded with a Finnigan MAT 95 SQ or a Varian MAT 771 spectrometer using the electronic impact technique (EI) with an ionization energy of 70 eV or by using the fast atom bombardment (FAB) technique with caesium. IR spectra were obtained with a Perkin-Elmer 881 or Nicolet Magna 750 spectrometer. Melting points were determined with a Leica Galen III instrument and are uncorrected. Elemental analyses were carried out with an Elementar vario EL apparatus.

**Catalysis**: **General procedure for the zinc-catalyzed hydroamination reaction**: A predried NMR tube was charged with the aminoalkene (430 μmol). A solution of the catalyst (11 μmol, 2.5 mol%) and [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (9 mg, 11 μmol, 2.5 mol%) in $C_6D_6$ (0.5 mL) was added under nitrogen. The NMR tube was flame-sealed under vacuum. The reaction mixture was then heated to 80 °C for the stated time. The reaction progress was monitored by $^1$H NMR spectroscopy. When the reaction was judged to be complete, the crude reaction mixture was subjected to column chromatography on silica gel.

**Ligand synthesis**

**General procedure A for the synthesis of 2-(alkylamino)tropones**: 2-Tosyloxytropone[13] (2.73 g, 10.0 mmol) was added in one portion to the neat amine (15 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred overnight. All volatiles were removed under reduced pressure and the oily residue was taken up in 2 N NaOH (15 mL) and $CH_2Cl_2$ (30 mL). The aqueous phase was extracted with $CH_2Cl_2$ (2× 30 mL). The combined organic phases were washed with brine (20 mL) and dried with $MgSO_4$. The crude product was purified by flash column chromatography ($SiO_2$).

**General procedure B for the synthesis of 2-(alkylamino)tropones**: 2-Tosyloxytropone[23] (2.73 g, 10.0 mmol), the corresponding amine (12.6 mmol), and triethylamine (1.53 g, 15.1 mmol) were dissolved in ethanol (25 mL). The mixture was refluxed for 6 h and then cooled to room temp. All volatiles were removed under reduced pressure and the oily residue was taken up in 2 N NaOH (15 mL) and $CH_2Cl_2$ (30 mL). The aqueous phase was extracted twice with $CH_2Cl_2$ (30 mL). The combined organic phases were washed with brine (20 mL) and dried with $MgSO_4$. The crude product was purified by flash column chromatography ($SiO_2$).

**General procedure C for the synthesis of *N*,*N*′-dialkylaminotroponimines**: $Et_3OBF_4$ (1.75 g, 9.21 mmol) was dissolved in $CH_2Cl_2$ (10 mL). A solution of the 2-(alkylamino)tropone (9.20 mmol) in $CH_2Cl_2$ (10 mL) was slowly added. The solution was stirred at room temperature for 3 h, cooled to 0 °C, and the corresponding amine (20 mL) was then slowly added. The solution was allowed to warm to room temperature and stirred overnight. All volatiles were removed under reduced pressure and the oily residue was taken up in 2 N NaOH (10 mL) and $CH_2Cl_2$ (20 mL). The aqueous phase was extracted twice with $CH_2Cl_2$ (20 mL). The combined organic phases were washed with brine (20 mL) and dried with $MgSO_4$. The crude product was purified by flash column chromatography ($SiO_2$).

**General procedure D for of the synthesis of *N*,*N*′-dialkylaminotronimines**: $Et_3OBF_4$ (620 mg, 3.26 mmol) was dissolved in $CH_2Cl_2$ (5 mL). A solution of the 2-alkylaminotropone (3.04 mmol) in $CH_2Cl_2$ (5 mL) was slowly added. The solution was stirred at room temperature for 3 h and then all volatiles were removed in vacuo. The residue was taken up in ethanol (15 mL) and the corresponding amine (7.91 mmol) was added. The mixture was stirred at room temperature until TLC analysis showed completion of the reaction. Then all volatiles were removed under reduced pressure, the oily residue was taken up in 2 N NaOH (10 mL) and $CH_2Cl_2$ (20 mL). The aqueous phase was extracted with $CH_2Cl_2$ (2× 20 mL). The combined organic phases were washed with brine (20 mL) and dried with $MgSO_4$. The crude product was purified by flash column chromatography ($SiO_2$).

**2-(Methylamino)tropone (1a)**: Compound **1a** was prepared in accord with a modified literature procedure in 70% yield.[24]

**2-(Isopropylamino)tropone (2a)**: Compound **2a** was prepared in accord with a modified literature procedure in 89% yield.[20]

**2-(Cyclohexylamino)tropone (3a)**: Preparation according to general procedure A afforded **3a** as a yellow solid in 92% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.23–1.46 (m, 5H), 1.64–1.72 (m, 1H), 1.76–1.86 (m, 2H), 2.01–2.10 (m, 2H), 3.45–3.55 (m, 1H), 6.58 (d, $J$ = 10.8 Hz, 1H), 6.64 (t, $J$ = 9.4 Hz, 1H), 7.15 (t, $J$ = 12.4 Hz, 1H), 7.21–7.37 ppm (m, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 24.7, 25.6, 32.1, 51.1, 108.8, 121.7, 128.1, 136.2, 137.1, 154.6 ($C_q$), 176.4 ppm ($C_q$). MS (EI, 70 eV): $m/z$ (%): 203 (100) [$M^+$], 160 (37), 146 (39), 121 (40), 98 (38), 93 (65), 55 (23). HRMS: calcd for $C_{13}H_{17}NO$: 203.1310; found: 203.1309. Elemental analysis calcd (%) for $C_{13}H_{17}NO$: C 76.81, H 8.43, N 6.85; found: C 76.60, H 8.23, N 7.12.

**2-(Cyclododecylamino)tropone (5a)**: Preparation according to general procedure B afforded **5a** as a pale brownish solid in 74% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.32–1.52 (m, 18H), 1.53–1.64 (m, 2H), 1.70–1.82 (m, 2H), 3.69–3.79 (m, 1H), 6.55 (d, $J$ = 10.6 Hz, 1H), 6.63 (t, $J$ = 9.4 Hz, 1H), 7.12 (d, $J$ = 11.3 Hz, 1H), 7.19–7.31 ppm (m, 2H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 21.2, 23.2, 23.3, 23.8, 24.1, 29.1, 49.1, 108.5, 121.6, 127.9, 136.3, 137.1, 155.1 ($C_q$), 176.5 ppm ($C_q$). MS (EI, 70 eV): $m/z$ (%): 287 (100) [$M^+$], 244 (22), 160 (34), 146 (28), 133 (29), 132 (29), 122 (20), 121 (39), 93 (26), 84 (22), 55 (24). HRMS: calcd for $C_{19}H_{29}NO$: 287.2249; found: 287.2251.

**2-(1-Ethylpropylamino)tropone (6a)**: Preparation according to general procedure B afforded **6a** as a yellow solid in 92% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 0.94 (t, $J$ = 7.5 Hz, 6H), 1.55–1.78 (m, 4H), 3.44–3.53 (m, 1H), 6.56–6.68 (m, 2H), 7.11–7.19 (m, 1H), 7.20–7.28 ppm (m, 2H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 10.3, 26.7, 55.2, 108.8, 121.7, 127.8, 136.3, 137.1, 155.7 ($C_q$), 176.4 ppm ($C_q$). MS (EI, 70 eV): $m/z$ (%): 191 (41) [$M^+$], 163 (11), 162 (100), 105 (12), 77 (12). HRMS: calcd for $C_{12}H_{17}NO$: 191.1310; found: 191.1311.

**2-(Benzylamino)tropone (7a)**: Preparation according to general procedure A afforded **7a** as pale yellow crystals in 73% yield. M.p. 124 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 4.56 (d, $J$ = 6.0 Hz, 2H), 6.53 (d, $J$ = 10.4 Hz, 1H), 6.69 (t, $J$ = 9.4 Hz, 1H), 7.14–7.37 (m, 8H), 7.60 ppm (brs, 1H; NH). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 47.0, 109.1, 122.7, 127.3, 127.8, 128.9, 129.2, 136.2, 136.4 ($C_q$), 137.4, 155.4 ($C_q$), 177.0 ppm ($C_q$). MS (EI, 70 eV): $m/z$ (%): 211 (100) [$M^+$], 210 (17), 106 (40), 91 (94), 77 (11), 65 (21). HRMS: calcd for $C_{14}H_{13}NO$: 211.0997; found: 211.0991. Elemental analysis calcd (%) for $C_{14}H_{13}NO$: C 79.59, H 6.20, N 6.63; found: C 79.38, H 6.21, N 6.60.

**2-(2-Methoxyethylamino)tropone (8a)**: Preparation according to general procedure A afforded **8a** in 94% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.99 (pent., $J$ = 5.9 Hz, 2H), 3.35 (s, 3H), 3.43 (q, $J$ = 6.1 Hz, 2H), 3.49 (t, $J$ = 5.9 Hz, 2H), 6.56 (d, $J$ = 10.4 Hz, 1H), 6.65 (t, $J$ = 9.5 Hz, 1H), 7.13 (d, $J$ = 11.3 Hz, 1H), 7.18–7.28 (m, 2H), 7.41 ppm (brs, 1H; NH). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 28.6, 40.2, 58.8, 70.0, 108.5, 122.0, 128.4, 136.3, 137.2, 155.8 ($C_q$), 176.7 ppm ($C_q$). MS (EI, 70 eV): $m/z$ (%): 193 (66) [$M^+$], 149 (10), 148 (100), 135 (20), 134 (48), 106 (19), 105 (14), 77 (18). HRMS: calcd for $C_{11}H_{15}NO_2$: 193.1103; found: 193.1103.

**2-(3-Methoxypropylamino)tropone (9a)**: Preparation according to general procedure A afforded **9a** in 92% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 3.40 (s, 3H), 3.49 (q, $J$ = 5.5 Hz, 2H), 3.68 (t, $J$ = 5.5 Hz, 2H), 6.54 (d, $J$ = 10.3 Hz, 1H), 6.67 (t, $J$ = 9.4 Hz, 1H), 7.14 (d, $J$ = 11.3 Hz, 1H), 7.21 (t, $J$ = 10.3 Hz, 1H), 7.22–7.28 (m, 1H), 7.40 ppm (brs, 1H; NH). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 42.6, 59.0, 70.0, 108.5, 122.3, 128.9, 136.1, 137.2, 155.6 ($C_q$), 176.8 ppm ($C_q$). MS (EI, 70 eV): $m/z$ (%): 179 (39) [$M^+$], 134 (100), 106 (23), 84 (23). HRMS: calcd for $C_{10}H_{13}NO_2$: 179.0946; found: 179.0942.

**2-(Phenylamino)tropone (10a)**: Compound **10a** was prepared in accord with a slightly modified literature procedure in 94% yield.[3]

***N*-Methyl-2-(methylamino)troponimine [(Me)$_2$ATI]H (1b)**: Compound **1b** was prepared in accord with a modified literature procedure in 50% yield.[24]

***N*-Isopropyl-2-(isopropylamino)troponimine [(*i*Pr)$_2$ATI]H (2b)**: Compound **2b** was prepared in accord with a modified literature procedure in 83% yield.[20]

***N*-Cyclohexyl-2-(cyclohexylamino)troponimine [(Cy)$_2$ATI]H (3b)**: Preparation according to general procedure C afforded **3b** as a yellow oil in 90% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.24–1.47 (m, 10H), 1.60–1.68 (m, 2H), 1.72–1.82 (m, 4H), 1.84–1.95 (m, 4H), 3.47–3.55 (m, 2H), 6.05 (t, $J$ = 9.2 Hz, 1H), 6.29 (d, $J$ = 11.6 Hz, 2H), 6.65–6.71 (m, 2H), 7.88 ppm (brs, 1H; NH). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 24.8, 26.0, 26.9, 32.9, 53.5, 109.7, 116.9, 132.4, 151.4 ppm ($C_q$). MS (EI, 70 eV): $m/z$ (%): 284 (58) [$M^+$], 241 (17), 213 (17), 201 (100), 131 (19), 73 (54). HRMS: calcd for $C_{19}H_{28}N_2$: 284.2252; found: 284.2256. Elemental analysis calcd (%) for $C_{19}H_{28}N_2$: C 80.23, H 9.92, N 9.85; found: C 79.92, H 9.98, N 9.51.

***N*-Isopropyl-2-(cyclohexylamino)troponimine [(Cy/*i*Pr)ATI]H (4b)**: Preparation from **3a** by the reaction of isopropylamine according to general procedure C afforded **4b** as a yellow oil in 72% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.24 (d, $J$ = 6.3 Hz, 6H), 1.27–1.47 (m, 5H), 1.61–1.69 (m, 1H), 1.74–1.83 (m, 2H), 1.88–1.97 (m, 2H), 3.50 (sept., $J$ = 4.1 Hz, 1H), 3.82 (sept., $J$ = 6.3 Hz, 1H), 6.06 (t, $J$ = 9.2 Hz, 1H), 6.28 (d, $J$ = 11.2 Hz, 2H), 6.66–6.71 (m, 2H), 7.77 ppm (brs, 1H; NH). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 23.0, 24.9, 26.0, 32.9, 45.9, 53.5, 109.5, 110.0, 117.0, 132.4, 132.5, 151.3 ($C_q$), 151.6 ppm ($C_q$). MS (EI, 70 eV): $m/z$ (%): 244 (88) [$M^+$], 229 (52), 201 (100), 161 (61), 147 (20), 132 (24), 131 (30). HRMS: calcd for $C_{16}H_{24}N_2$: 244.1939; found: 244.1944. Elemental analysis calcd (%) for $C_{16}H_{24}N_2$: C 78.64, H 9.90, N 11.46; found: C 78.56, H 9.83, N 11.65.

***N*-Cyclododecyl-2-(cyclododecylamino)troponimine [(cyDod)$_2$ATI]H (5b)**: Preparation according to general procedure D afforded **5b** as yellow crystals (ethanol) in 74% yield. M.p. 128 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 1.29–1.55 (m, 42H), 1.63–1.74 (m, 2H), 3.67–3.74 (m, 2H), 6.04 (t, $J$ = 9.2 Hz, 1H), 6.25 (d, $J$ = 11.2 Hz, 2H), 6.65–6.73 (m, 2H), 7.93 ppm (brs, 1H; NH). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 21.3, 23.2, 23.3, 24.3, 24.6, 29.7, 51.6, 109.3, 116.6, 132.4, 151.7 ppm ($C_q$). MS (EI, 70 eV): $m/z$ (%): 452 (100) [$M^+$], 298 (35), 297 (32), 285 (89), 132 (34), 131 (64). HRMS: calcd for $C_{31}H_{52}N_2$: 452.4130; found: 452.4134. Elemental analysis calcd (%) for $C_{31}H_{52}N_2$: C 82.24, H 11.58, N 6.19; found: C 82.02, H 11.40, N 6.69.

***N*-(1-Ethylpropyl)-2-(1-ethylpropylamino)troponimine [(*i*Pent)$_2$ATI]H (6b)**: Preparation according to general procedure C afforded **6b** as a yellow solid in 88% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 0.87 (t, $J$ = 7.4 Hz, 12H), 1.48–1.68 (m, 8H), 3.46 (pent., $J$ = 6.0 Hz, 2H), 6.03 (t, $J$ = 9.1 Hz, 1H), 6.28 (d, $J$ = 11.2 Hz, 2H), 6.63–6.70 (m, 2H), 7.96 ppm (brs, 1H; NH). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 10.5, 27.5, 57.2, 109.4, 116.6, 132.3, 152.1 ppm ($C_q$). MS (EI, 70 eV): $m/z$ (%): 261 (28) [$M^+$], 260 (25), 232 (77), 131 (100), 161 (30), 132 (38), 131 (77). HRMS: calcd for $C_{17}H_{28}N_2$: 261.2331; found: 261.2330.

***N*-Benzyl-2-(benzylamino)troponimine [(Bn)$_2$ATI]H (7b)**: Preparation according to general procedure D afforded **7b** as a yellow solid in 74% yield. M.p. 76 °C. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 4.75 (s, 4H), 6.52 (brs, 1H), 6.65 (brs, 2H), 7.04 (brs, 2H), 7.22–7.42 ppm (m, 10H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 49.6, 114.1 (brs), 122.1 (brs), 127.3, 128.5, 128.6, 136.0 (brs), 137.7 (brs, $C_q$), 153.0 ppm ($C_q$). MS (EI, 70 eV): $m/z$ (%): 300 (17) [$M^+$], 209 (100), 106 (24), 91 (78), 65 (16). HRMS: calcd for $C_{19}H_{24}N_2$: 310.1626; found: 310.1630.

***N*-(2-Methoxyethyl)-2-(2-methoxyethylamino)troponimine [(C$_2$OMe)$_2$ATI]H (8b)**: Preparation according to general procedure C afforded **8b** as a brown oil in 59% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 3.43 (s, 6H), 3.50 (t, $J$ = 6.0 Hz, 4H), 3.73 (t, $J$ = 6.0 Hz, 4H), 6.18 (t, $J$ = 9.4 Hz, 1H), 6.31 (d, $J$ = 10.5 Hz, 2H), 6.74–6.81 ppm (m, 2H). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 46.1, 59.0, 72.1, 110.6, 118.4, 133.3, 153.4 ppm ($C_q$). MS (EI, 70 eV): $m/z$ (%): 236 (19) [$M^+$], 191 (100), 134 (17), 131 (18). HRMS: calcd for $C_{13}H_{20}N_2O_2$: 236.1525; found: 236.1522.

***N*-(3-Methoxypropyl)-2-(3-methoxypropylamino)troponimine [(C$_3$OMe)$_2$ATI]H (9b)**: Preparation according to general procedure C afforded **9b** as a brown oil in 83% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 2.01 (pent., $J$ = 6.5 Hz, 4H), 3.36 (s, 6H), 3.40 (t, $J$ = 6.8 Hz, 2H), 3.53 (t, $J$ = 6.2 Hz, 2H), 6.13 (t, $J$ = 9.2 Hz, 1H), 6.29 (d, $J$ = 10.8 Hz, 2H), 6.71–6.78 (m, 2H), 7.75 ppm (brs, 1H; NH). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 30.2, 43.3, 58.7, 71.0, 110.2, 117.7, 133.0, 153.1 ppm ($C_q$). MS (EI, 70 eV):

*m/z* (%): 264 (62) [$M^+$], 205 (100), 191 (75), 133 (40), 132 (31), 131 (54). HRMS: calcd for $C_{15}H_{24}N_2O_2$: 264.1838; found: 264.1837.

***N*-Phenyl-2-(phenylamino)troponimine [(Ph)$_2$ATI]H (10b)**: Compound **10b** was prepared in accord with a literature procedure in 35% yield.[3]

***N*-Isopropylamino-2-(phenylamino)troponimine [(*i*Pr/Ph)ATI]H (11b)**: Preparation from **3a** by the reaction of isopropylamine according to general procedure C afforded **4b** as a yellow oil in 80% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta = 1.36$ (d, $J = 6.4$ Hz, 6H), 3.84–3.94 (m, 1H), 6.19–6.26 (m, 2H), 6.59–6.73 (m, 3H), 6.84–6.91 (m, 2H), 7.04 (tt, $J = 1.1$, $J = 7.4$ Hz, 1H), 7.32–7.39 (m, 2H), 7.56 ppm (brs, 1H; NH). $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta = 22.3$, 43.8, 105.2, 111.9, 119.1, 120.4, 121.0, 122.5, 133.1, 133.9, 150.1 ($C_q$), 151.6 ($C_q$), 155.0 ppm ($C_q$). MS (EI, 70 eV): *m/z* (%): 238 (22) [$M^+$], 180 (81), 149 (26), 134 (100), 106 (77), 104 (31), 77 (76). HRMS: calcd for $C_{16}H_{18}N_2$: 238.1470; found: 238.1470. Elemental analysis calcd (%) for $C_{16}H_{18}N_2$: C 80.63, H 7.61, N 11.75; found: C 80.27, H 7.72, N 12.17.

**Synthesis of the metal complexes**

**General procedure E**: A solution of the corresponding aminotroponimine (1.1 mmol) in toluene (10 mL) was slowly added to a solution of $ZnMe_2$ (1.2 M in toluene, 1.0 mL, 1.2 mmol) in toluene (10 mL). The solution was stirred at room temperature for 3 h. The reaction was judged to be complete when gas evolution had ceased. All volatiles were removed under reduced pressure and the yellow residue was washed twice with pentane (5 mL).

**General procedure F**: A solution of the aminotroponimine (1.1 mmol) in toluene (10 mL) was slowly added to a solution of $ZnEt_2$ (1.0 M in toluene, 0.6 mL, 0.6 mmol) in toluene (10 mL). The solution was stirred at room temperature for 3 h. The reaction was judged to be complete when the evolution had ceased. All volatiles were removed under reduced pressure and the yellow residue was washed twice with pentane (5 mL).

**Bis[*N*-Methyl-2-(methylamino)troponiminato]zinc [{(Me)$_2$ATI}$_2$Zn] (1c)**: Preparation from **1b** according to general procedure F afforded **1c** in 61% yield. X-ray quality crystals could be grown from dichloromethane at −40 °C. $^1$H NMR ($C_6D_6$, 500 MHz): $\delta = 2.92$ (s, 12H), 6.30 (t, $J = 9.0$ Hz, 2H), 6.42 (d, $J = 11.4$ Hz, 4H), 6.97 ppm (t, $J = 9.3$ Hz, 4H). $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta = 37.9$, 111.0, 116.1, 135.0, 162.2 ppm. MS (EI, 80 eV): *m/z* (%): 358 (18) [$M^+$], 148 (16), 145 (75), 133 (57), 106 (100). HRMS: calcd for $C_{19}H_{28}N_2Zn$: 358.113591; found: 358.11337.

**Bis[*N*-isopropyl-2-(isopropylamino)troponiminato]zinc [{(*i*Pr)$_2$ATI}$_2$Zn] (2c)**: Preparation from **2b** according to general procedure F afforded **2c** in 97% yield. $^1$H NMR ($C_6D_6$, 500 MHz): $\delta = 1.17$ (d, $J = 6.3$ Hz, 24H), 3.81 (sept., $J = 6.3$ Hz, 4H), 6.23 (t, $J = 9.1$ Hz, 2H), 6.48 (d, $J = 11.7$ Hz, 4H), 6.93 ppm (t, $J = 9.1$ Hz, 4H). $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta = 24.0$, 48.3, 112.1, 115.4, 134.6, 160.0 ppm. MS (EI, 80 eV): *m/z* (%): 470 (100) [$M^+$], 455 (74), 427 (41), 267 (11), 235 (14), 187 (44), 145 (44). HRMS calcd for $C_{26}H_{38}N_4Zn$: 470.23879; found: 470.23859.

**[*N*-Cyclohexyl-2-(cyclohexylamino)troponiminato]methylzinc [{(Cy)$_2$ATI}ZnMe] (3c)**: Preparation from **3b** according to general procedure E afforded **3c** in 88% yield. X-ray quality crystals could be grown from toluene at −40 °C. $^1$H NMR ($C_6D_6$, 500 MHz): $\delta = 0.08$ (s, 3H), 1.05–1.91 (m, 20H), 3.50–3.59 (m, 2H), 6.38 (t, $J = 9.1$ Hz, 1H), 6.73 (d, $J = 11.6$ Hz, 2H), 6.99 ppm (dd, $J = 9.1$, $J = 11.7$ Hz, 2H). $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta = -9.7$, 25.7, 26.0, 35.2, 57.1, 111.3, 117.5, 134.1, 159.9 ppm. MS (EI, 80 eV): *m/z* (%): 362 (17) [$M^+$], 347 (11), 284 (29), 201 (100), 131 (82). Elemental analysis calcd (%) for $C_{20}H_{30}N_2Zn$: C 66.02, H 8.31, N 7.70; found: C 65.69, H 8.65, N 7.33.

**[*N*-Cyclohexyl-2-(isopropylamino)troponiminato]methylzinc [{(Cy/*i*Pr)ATI}ZnMe] (4c)**:[16b] Preparation from **4b** according to general procedure E afforded **4c** as a brown-yellow oil in 47% yield. $^1$H NMR ($C_6D_6$, 500 MHz): $\delta = 0.04$ (s, 3H), 1.14 (d, $J = 6.2$ Hz, 6H), 1.19 (d, $J = 13.0$ Hz, 1H), 1.34–1.52 (m, 5H), 1.62 (d, $J = 13.2$ Hz, 2H), 1.87 (d, $J = 11.5$ Hz, 2H), 3.53 (dt, $J = 3.1$, $J = 8.0$ Hz, 1H), 3.76 (sept., $J = 6.2$ Hz, 1H), 6.37 (t, $J = 9.2$ Hz, 1H), 6.59 (d, $J = 11.3$ Hz, 1H), 6.71 (t, $J = 11.5$ Hz, 1H), 7.00 ppm (m, 2H). $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta = -9.9$, 24.4, 25.9, 26.2, 35.4, 48.3, 57.3, 111.5, 111.6, 117.7, 134.4, 134.5, 160.1, 160.2 ppm. MS (EI, 80 eV): *m/z* (%): 322 (3) [$M^+$], 306 (14) [$M^+ - CH_3$], 322 (3), 244 (78), 229 (54), 201 (100), 161 (47). HRMS: calcd for $C_{17}H_{26}N_2Zn$: 322.13874; found: 322.13715.

**[*N*-Cyclododecyl-2-(cyclododecylamino)troponiminato]methylzinc [{(cyDod)$_2$ATI}ZnMe] (5c)**: Preparation from **5b** according to general procedure E afforded **5c** in 84% yield. X-ray quality crystals could be grown from dichloromethane at −40 °C. $^1$H NMR ($C_6D_6$, 500 MHz): $\delta = 0.13$ (s, 3H), 1.31–1.42 (m, 38H), 1.54–1.57 (m, 4H), 1.88–1.92 (m, 4H), 4.02 (m, 2H), 6.36 (t, $J = 9.0$ Hz, 1H), 6.92 (d, $J = 11.3$ Hz, 2H), 7.04 ppm (t, $J = 9.4$ Hz, 2H). $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta = -10.1$, 21.7, 23.3, 23.4, 24.2, 24.6, 31.3, 53.8, 111.3, 117.6, 134.3, 160.4 ppm. MS (EI, 80 eV): *m/z* (%): 530 (100) [$M^+$], 515 (43), 452 (69), 409 (14), 285 (46), 215 (36), 201 (33), 131 (25). HRMS: calcd for $C_{32}H_{54}N_2Zn$: 530.3578; found: 530.3576.

**[*N*-(1-Ethylpropyl)-2-(1-ethylpropylamino)troponiminato]methylzinc [{(*i*Pent)$_2$ATI}ZnMe] (6c)**: Preparation from **6b** according to general procedure E afforded **6c** as an orange oil in 97% yield. $^1$H NMR ($C_6D_6$, 500 MHz): $\delta = 0.00$ (s, 3H), 0.79 (t, $J = 7.4$ Hz, 12H), 1.60 (m, 8H), 3.54 (pent, $J = 6.4$ Hz, 4H), 6.35 (t, $J = 9.2$ Hz, 1H), 6.74 (d, $J = 11.6$ Hz, 2H), 6.96 ppm (t, $J = 9.0$ Hz, 2H). $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta = -10.8$, 11.0, 29.4, 59.9, 111.5, 117.9, 134.4, 161.4 ppm. MS (EI, 80 eV): *m/z* (%): 338 (15) [$M^+$], 309 (41), 260 (24), 231 (100), 201 (14), 189 (10), 161 (25), 131 (43). Elemental analysis calcd (%) for $C_{18}H_{30}N_2Zn$: C 63.62, H 8.90, N 8.24; found: C 63.69, H 8.81, N 8.21.

**[*N*-Benzyl-2-(benzylamino)troponiminato]methylzinc [{(Bn)$_2$ATI}ZnMe] (7c)**: A solution of aminotroponimine **7b** (1.8 mmol) in toluene (10 mL) was slowly added to a solution of $ZnMe_2$ (1.2 M in toluene, 2.0 mL, 2.4 mmol) in toluene (10 mL). After 30 min a solid began to precipitate from solution. The reaction mixture was stirred for 1 h then heated until a clear solution was observed. The solution was cooled to room temperature without stirring and then filtered. The filtered crystals were washed twice with pentane (5 mL). Yield: 88%. $^1$H NMR ($C_6D_6$, 500 MHz): $\delta = -1.08$ (s, 3H), 4.12 (s, 2H), 4.34 (s, 2H), 6.19–6.39 (m, 2H), 6.62 (d, $J = 11.2$ Hz, 1H), 6.81 (t, $J = 11.1$ Hz, 1H), 6.89–6.96 (m, 4H), 7.06–7.13 ppm (m, 7H). $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta = -14.1$, 54.2, 112.3, 116.3, 118.8, 126.9, 135.1, 139.7, 140.6, 161.0 ppm. Elemental analysis calcd (%) for $C_{22}H_{22}N_2Zn$: C 69.57, H 5.85, N 7.38%; found: C 70.12, H 5.87, N 7.11.

**Bis[*N*-(2-Methoxyethyl)-2-(2-methoxyethylamino)troponiminato]zinc [{(C$_2$OMe)$_2$ATI}$_2$Zn] (8c)**: A solution of aminotroponimine **8b** (2.1 mmol) in THF (10 mL) was slowly added to a solution of $ZnEt_2$ (1.0 M in toluene, 1.1 mL, 1.1 mmol) in toluene (10 mL) at −78 °C. The solution was slowly warmed to room temperature and stirred for 3 h. The reaction was judged to be complete when the gas evolution had stopped. All volatiles were removed under reduced pressure and the yellow residue was washed twice with pentane (5 mL). Yield: 85%. $^1$H NMR ($C_6D_6$, 500 MHz): $\delta = 2.82$ (s, 12H), 3.45 (s, 16H), 6.23 (t, $J = 9.9$ Hz, 2H), 6.42 (d, $J = 11.2$ Hz, 4H), 6.91 ppm (t, $J = 9.2$ Hz, 4H). $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta = 50.4$, 58.4, 72.6, 111.2, 115.5, 137.1, 161.4 ppm. MS (EI, 80 eV): *m/z* (%): 534 (46) [$M^+$], 502 (10), 489 (100), 304 (25), 239 (7). HRMS: calcd for $C_{26}H_{38}N_4O_4Zn$: 534.218451; found: 534.21844.

**Bis[*N*-(3-Methoxypropyl-2-(3-methoxypropylamino)troponiminato]zinc [{(C$_3$OMe)$_2$ATI}$_2$Zn] (9c)**: Preparation from **9b** according to general procedure F afforded **9c** in 75% yield. X-ray quality crystals can be grown from hot toluene. $^1$H NMR ($C_6D_6$, 500 MHz): $\delta = 1.91$–1.98 (m, 8H), 3.00 (s, 12H), 3.09 (t, $J = 5.8$ Hz, 8H), 3.51 (m, 8H), 6.22 (t, $J = 9.2$ Hz, 2H), 6.57 (d, $J = 11.2$ Hz, 4H), 6.91 ppm (dd, $J = 9.1$ Hz, 4H). $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta = 31.8$, 47.7, 57.9, 70.5, 111.6, 116.0, 134.9, 161.0 ppm. MS (EI, 80 eV): *m/z* (%): 590 (37) [$M^+$], 327 (100), 269 (10), 203 (24), 131 (9). Elemental analysis calcd (%) for $C_{30}H_{46}N_4O_4Zn$: C 60.85, H 7.83, N 9.46; found C 60.54, H 7.74, N 9.07.

**Bis[*N*-phenyl-2-(phenylamino)troponiminato]zinc [{(Ph)$_2$ATI}$_2$Zn] (10c)**: Preparation from **10b** according to general procedure F afforded **10c** in 97% yield. X-ray quality crystals could be grown from toluene at −40 °C. $^1$H NMR ($C_6D_6$, 500 MHz): $\delta = 6.05$ (t, $J = 9.2$ Hz, 2H), 6.44–6.50 (m, 4H), 6.90–6.95 (m, 8H), 7.03–7.06 (m, 8H), 7.16–7.20 ppm (m, 8H). $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta = 116.7$, 120.1, 123.9, 124.3, 129.7, 134.9, 149.7, 160.5 ppm. MS (EI, 80 eV): *m/z* (%): 606 [$M^+$] (80), 303 (10), 272 (100), 245 (9), 169 (13). HRMS: calcd for $C_{38}H_{30}N_4Zn$: 606.176191; found: 606.17654.

**Bis[*N*-Phenyl-2-(isopropylamino)troponiminato]zinc [{(Ph/*i*Pr)ATI}$_2$Zn] (11c)**: Preparation from **11b** according to general procedure E afforded **11c** in 55%. $^1$H NMR ($C_6D_6$, 500 MHz): $\delta$ = 0.97 (d, $J$ = 6.1 Hz, 6H), 1.20 (d, $J$ = 6.2 Hz, 6H), 3.72 (sept., $J$ = 6.3 Hz, 2H), 6.18 (t, $J$ = 9.1 Hz, 2H), 6.52 (d, $J$ = 11.6 Hz, 2H), 6.62 (t, $J$ = 10.1 Hz, 2H), 6.82 (m, 4H), 7.17 (m, 4H), 7.07 ppm (m, 6H). $^{13}$C NMR ($C_6D_6$, 125 MHz): $\delta$ = 23.0, 23.9, 48.1, 114.25, 114.5, 118.1, 123.3, 124.0, 129.6, 134.66, 134.8, 149.9, 159.6, 160.5 ppm. MS (EI, 80 eV): $m/z$ (%): 538 (2) [$M^+$], 238 (17), 149 (42), 134 (100), 106 (59). HRMS: calcd for $C_{32}H_{34}N_4Zn$ (540.03): 538.20749; found: 538.20782.

**X-ray crystallographic studies on 1c, 3c, 5c, and 7c–10c**: Crystals of **1c**, **3c**, **7c**, **9c**, and **10c** were grown from toluene. Crystals of **5c** were obtained from dichloromethane and **8c** from pentane. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the −73 °C $N_2$ cold stream of a Stoe IPDS II 2T diffractometer. Subsequent computations were carried out with an Intel Pentium IV PC.

All structures were solved by Patterson or direct methods (SHELXS-97[29]). 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 $F$, 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, using the program SHELXL-97.[30] Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon atom to which they are bonded by assuming a C–H bond length of 0.95 Å. The hydrogen atom contributions were calculated but not refined. The locations of the largest peaks in the final difference Fourier map and the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, bond lengths and angles have been deposited as Supporting Information.

CCDC-609557 (**3c**), -630411 (**1c**), -630412 (**5c**), -630413 (**7c**), -630414 (**8c**), -630415 (**9c**), and -630416 (**10c**) 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.

**Complex 1c**: $C_{18}H_{22}N_2Zn$, $M$ = 359.77, orthorhombic space group *Pbcn*, $a$ = 1391.10(14), $b$ = 1846.1(2), $c$ = 662.16(9) pm, $V$ = 1700.5(3) × 10$^6$ pm$^3$, $T$ = 200(2) K, $Z$ = 4, $\mu(Mo_{K\alpha})$ = 1.449 mm$^{-1}$, $\theta_{max}$ = 25°, 1496 [$R_{int}$ = 0.0632] independent reflections measured, of which 1083 were considered observed with $I > 2\sigma(I)$, max. and min. residual electron densities 0.436 and −0.574 e A$^{-3}$, 107 parameters, $R1$ ($I > 2\sigma(I)$) = 0.0379, $wR_2$ (all data) = 0.0970.

**Complex 3c**: $C_{20}H_{30}N_2Zn$, $M$ = 363.83, triclinic space group $P\bar{1}$, $a$ = 973.58(7), $b$ = 1100.97(8), $c$ = 2007.60(13) pm, $\alpha$ = 76.685(5), $\beta$ = 86.477(6), $\gamma$ = 64.209(5)°, $V$ = 1883.6(2) × 10$^6$ pm$^3$, $T$ = 200(2) K, $Z$ = 4, $\mu(Mo_{K\alpha})$ = 1.306 mm$^{-1}$, $\theta_{max}$ = 25°, 6621 [$R_{int}$ = 0.0553] independent reflections measured of which 5389 were considered observed with $I > 2\sigma(I)$, max. and min. residual electron densities 0.370 and −0.359 e A$^{-3}$, 417 parameters, $R_1$ [$I > 2\sigma(I)$] = 0.0341, $wR_2$ (all data) = 0.0874.

**Complex 5c**: $C_{33}H_{56}N_2Cl_2Zn$, $M$ = 617.07, triclinic, space group $P\bar{1}$, $a$ = 888.04(11), $b$ = 1101.09(10), $c$ = 1798.35(2) pm, $\alpha$ = 101.462(8), $\beta$ = 103.789(9), $\gamma$ = 97.943(9)°, $V$ = 1641.6(3) × 10$^6$ pm$^3$, $T$ = 200(2) K, $Z$ = 2, $\mu(Mo_{K\alpha})$ = 0.934 mm$^{-1}$, $\theta_{max}$ = 29.5°, 5746 [$R_{int}$ = 0.0498] independent reflections measured of which 4539 were considered observed with $I > 2\sigma(I)$, max. and min. residual electron densities 0.964 and −0.726 e A$^{-3}$, 344 parameters, $R_1$ [$I > 2\sigma(I)$] = 0.0464; $wR_2$ (all data) = 0.1214.

**Complex 7c**: $C_{22}H_{22}N_2Zn$, $M$ = 379.79, orthorhombic, space group *Pbcn*, $a$ = 626.46(5), $b$ = 2093.38(2), $c$ = 1392.52(14) pm, $V$ = 1826.6(3) × 10$^6$ pm$^3$, $T$ = 200(2) K, $Z$ = 4, $\mu(Mo_{K\alpha})$ = 1.350 mm$^{-1}$, $\theta_{max}$ = 29.2°, 2433 [$R_{int}$ = 0.0378] independent reflections measured of which 1605 were considered observed with $I > 2\sigma(I)$, max. and min. residual electron densities 0.242 and −0.337 e A$^{-3}$, 116 parameters, $R_1$ [$I > 2\sigma(I)$] = 0.0301; $wR_2$ (all data) = 0.0659.

**Complex 8c**: $C_{26}H_{38}N_4O_4Zn$, $M$ = 535.97, triclinic space group $P\bar{1}$, $a$ = 966.14(2), $b$ = 1033.3(2), $c$ = 1471.4(3) pm, $\alpha$ = 98.89(3), $\beta$ = 95.52(3), $\gamma$ = 111.38(3)°, $V$ = 1332.7(5) × 10$^6$ pm$^3$, $T$ = 200(2) K, $Z$ = 2, $\mu(Mo_{K\alpha})$ = 0.959 mm$^{-1}$, $\theta_{max}$ = 25.0°, 4699 [$R_{int}$ = 0.0566] independent reflections measured of which 3625 were considered observed with $I > 2\sigma(I)$, max. and min. residual electron densities 0.395 and −0.408 e A$^{-3}$, 320 parameters, $R_1$ [$I > 2\sigma(I)$] = 0.0348, $wR_2$ (all data) = 0.0734.

**Complex 9c**: $C_{30}H_{46}N_4O_4Zn$, $M$ = 592.10, tetragonal, space group $I4_1/a$, $a$ = 1333.30(14), $c$ = 1754.11(14) pm, $V$ = 3118.3(5) × 10$^6$ pm$^3$, $T$ = 200(2) K, $Z$ = 4, $\mu(Mo_{K\alpha})$ = 0.826 mm$^{-1}$, $\theta_{max}$ = 29.2°, 2111 [$R_{int}$ = 0.0391] independent reflections measured of which 1790 were considered observed with $I > 2\sigma(I)$, max. and min. residual electron densities 0.258 and −0.277 e A$^{-3}$, 90 parameters, $R_1$ [$I > 2\sigma(I)$] = 0.0300, $wR_2$ (all data) = 0.0757.

**Complex 10c**: $C_{38}H_{30}N_4Zn$, $M$ = 608.05, monoclinic space group $P2_1/c$, $a$ = 1213.17(10), $b$ = 1662.63(14), $c$ = 1723.14(15) pm, $\beta$ = 120.648(6), $V$ = 2990.2(5) × 10$^6$ pm$^3$, $T$ = 200(2) K, $Z$ = 4, $\mu(Mo_{K\alpha})$ = 0.855 mm$^{-1}$, $\theta_{max}$ = 29.5°, 5233 [$R_{int}$ = 0.0354] independent reflections measured of which 3934 were considered observed with $I > 2\sigma(I)$, max. and min. residual electron densities 0.227 and −0.302 e A$^{-3}$, 388 parameters, $R_1$ [$I > 2\sigma(I)$] = 0.0304; $wR_2$ (all data) = 0.0589.

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