ORGANOMETALLICS
Article

Organometallics **2010,** *29,* 2637–2645 2637
DOI: 10.1021/om901012f

Functionalized Aminotroponiminate Zinc Complexes as Catalysts for the Intramolecular Hydroamination of Alkenes

Maximilian Dochnahl,[†,‡] Karolin Löhnwitz,[§] Anja Lühl,[§] Jens-Wolfgang Pissarek,[†] Mustafa Biyikal,[†] Peter W. Roesky,*[,§] and Siegfried Blechert*[,†]

[†]*Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin, Germany, and* [§]*Institut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT), Engesserstrasse 15, 76131 Karlsruhe, Germany.* [‡]*Present address: BASF SE, Global Research Crop Protection, 67056 Ludwigshafen, Germany*

Received November 23, 2009

Substituted aminotroponimines, {R-ATI(iPr)$_2$}H (R = Br, I, PhN$_2$, NO$_2$, PhS, PhSe, PhTe, 3,5-(CF$_3$)$_2$-C$_6$H$_3$S, PhS(O)), bearing different functional groups in the 5-position were prepared. Reaction of these compounds with ZnMe$_2$ in toluene at 0 °C delivered the corresponding methyl zinc complexes [{R-ATI(iPr)$_2$}ZnMe] in high yields. The solid state structures of four selected examples were established via single-crystal X-ray diffraction analysis. In all compounds the zinc atoms are coordinated in a trigonal-planar fashion. All complexes were investigated as catalysts in the intramolecular hydroamination of non-activated alkenes. The attachment of electron-withdrawing groups in the 5-position such as nitro-or sulfoxide decreased the activity of the corresponding zinc catalysts. In contrast, donor substituents such as a thioether moiety at the backbone of the ligand increased the stability of the chelate and also rendered the zinc atom more reactive. On the other hand, the 5-brominated compound is very labile under the catalytic conditions used. In order to study the potential of an additional beneficial effect from the steric environment around the zinc atom on both reactivity and stability of the corresponding complexes, a prototypic ligand bearing a 5-phenylsulfanyl substituent at the backbone and two cyclohexyl substituents at the nitrogen atoms, {PhS-ATI(Cy)$_2$}H, and its corresponding zinc complex, [{PhS-ATI(Cy)$_2$}ZnMe], were synthesized.

Introduction

Aminotroponiminates ((R$_2$)ATIs) are a well established class of ligands, which were introduced into coordination chemistry in the 1960s by researchers from DuPont.[1−4] Like 1,4-diazabutadiene, {(R)$_2$ATI}$^-$ can form five-membered metallacycles upon coordination to a metal atom. Today it is well established that aminotroponimines can act as ligands for a wide range of main group elements and transition and f-block metals.[5] The corresponding deprotonated aminotroponiminates usually act as bidentate, monoanionic ligands containing a 10 π-electron backbone (Scheme 1). In most of the reports only simple {(R)$_2$ATI}$^-$ systems were used, in which the R group usually is methyl or isopropyl.

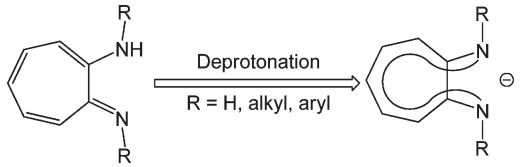
Recently, we have shown that *N*-isopropyl-2-(isopropylamino)troponiminate zinc methyl, [{H-ATI(iPr)$_2$}ZnMe] (**I**), is a highly active precatalyst for the hydroamination of alkenes and alkynes.[6,7] The formed zinc catalyst shows, besides its good catalytic activity and selectivity, high tolerance toward polar functional groups and high stability toward air and moisture.[8−14] These advantages make zinc complexes an attractive alternative to the previously used catalysts for

*Corresponding authors. E-mail: roesky@kit.edu; blechert@chem.tu-berlin.de.

(1) Brasen, W. R.; Holmquist, H. E.; Benson, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 995–956.
(2) Brasen, W. R.; Holmquist, H. E.; Benson, R. E. *J. Am. Chem. Soc.* **1961**, *83*, 3125–3135.
(3) Benson, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 5948–9.
(4) Phillips, W. D.; Benson, R. E. *J. Chem. Phys.* **1960**, *33*, 607–608.
(5) Roesky, P. W. *Chem. Soc. Rev.* **2000**, *29*, 335–345.
(6) Zulys, A.; Dochnahl, M.; Hollmann, D.; Löhnwitz, K.; Herrmann, J.-S.; Roesky, P. W.; Blechert, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 7794–7798.
(7) Löhnwitz, K.; Molski, M. J.; Lühl, A.; Roesky, P. W.; Dochnahl, M.; Blechert, S. *Eur. J. Inorg. Chem.* **2009**, 1369–1375.
(8) Meyer, N.; Löhnwitz, K.; Zulys, A.; Roesky, P. W.; Dochnahl, M.; Blechert, S. *Organometallics* **2006**, *25*, 3730–3734.
(9) Alex, K.; Tillack, A.; Schwarz, N.; Beller, M. *ChemSusChem* **2008**, *1*, 333–338.
(10) Horrillo-Martinez, P.; Hultzsch, K. C. *Tetrahedron Lett.* **2009**, *50*, 2054–2056.
(11) Okuma, K.; Seto, J.-I.; Sakaguchi, K.-I.; Ozaki, S.; Nagahora, N.; Shioji, K. *Tetrahedron Lett.* **2009**, *50*, 2943–2945.
(12) Prior, A. M.; Robinson, R. S. *Tetrahedron Lett.* **2008**, *49*, 411–414.
(13) Yin, Y.; Ma, W.; Chai, Z.; Zhao, G. *J. Org. Chem.* **2007**, *72*, 5731–5736.
(14) Biyikal, M.; Löhnwitz, K.; Roesky, P. W.; Blechert, S. *Synlett* **2008**, 3106–3110.
(15) Aillaud, I.; Collin, J.; Hannedouche, J.; Schulz, E. *Dalton Trans.* **2007**, 5105–18.
(16) Andrea, T.; Eisen, M. S. *Chem. Soc. Rev.* **2008**, *37*, 550–567.
(17) Beller, M.; Tillack, A.; Seayad, J. In *Transition Metal Organic Synthesis*, 2nd ed.; VCH: Weinheim, 2004; Vol. *2*, pp 403−414.
(18) Brunet, J.-J.; Neibecker, D. In *Catalytic Heterofunctionalization*; VCH: Weinheim, 2001; Vol. *1*, pp 91−141.
(19) Bytschkov, I.; Doye, S. *Eur. J. Org. Chem.* **2003**, 935–946.
(20) Doye, S. *Synlett* **2004**, 1653–1672.
(21) Hii, K. K. *Pure Appl. Chem.* **2006**, *78*, 341–349.
(22) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673–686.
(23) Hultzsch, K. C. *Org. Biomol. Chem.* **2005**, *3*, 1819–1824.
(24) Lee, A. V.; Schafer, L. L. *Eur. J. Inorg. Chem.* **2007**, 2243–2255.
(25) Mei, L. *Lett. Org. Chem.* **2008**, *5*, 174–190.
(26) Müller, T. E.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. *Chem. Rev.* **2008**, *108*, 3795–3892.

Published on Web 05/20/2010

Scheme 1



the hydroamination reaction[15−32] mainly based on lithium,[33] the alkaline earth metals,[34−39] the lanthanides,[40−69] group 4 metals,[19,70−90] the platinum metals (Rh,[91−97] Ir,[98,99] Pd,[100−107] Pt[108−113]), nickel,[114−116] copper,[117−121] silver,[122] and gold.[31,123−128]

(27) Odom, A. L. *Dalton Trans.* **2005**, 225–233.
(28) Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104–114.
(29) Seayad, J.; Tillack, A.; Hartung, C. G.; Beller, M. *Adv. Synth. Catal.* **2002**, *344*, 795–813.
(30) Severin, R.; Doye, S. *Chem. Soc. Rev.* **2007**, *36*, 1407–1420.
(31) Widenhoefer, R. A.; Han, X. *Eur. J. Org. Chem.* **2006**, 4555–4563.
(32) Roesky, P. W.; Müller, T. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 2708–2710.
(33) Martinez, P. H.; Hultzsch, K. C.; Hampel, F. *Chem. Commun.* **2006**, 2221–2223.
(34) Arrowsmith, M.; Hill, M. S.; Kociok-Kohn, G. *Organometallics* **2009**, *28*, 1730–1738.
(35) Barrett, A. G. M.; Boorman, T. C.; Crimmin, M. R.; Hill, M. S.; Kociok-Kohn, G.; Procopiou, P. A. *Chem. Commun.* **2008**, 5206–5208.
(36) Barrett, A. G. M.; Casely, I. J.; Crimmin, M. R.; Hill, M. S.; Lachs, J. R.; Mahon, M. F.; Procopiou, P. A. *Inorg. Chem.* **2009**, *48*, 4445–4453.
(37) Crimmin, M. R.; Casely, I. J.; Hill, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 2042–2043.
(38) Datta, S.; Roesky, P. W.; Blechert, S. *Organometallics* **2007**, *26*, 4392–4394.
(39) Lachs, J. R.; Barrett, A. G. M.; Crimmin, M. R.; Kociok-Kohn, G.; Hill, M. S.; Mahon, M. F.; Procopiou, P. A. *Eur. J. Inorg. Chem.* **2008**, 4173–4179.
(40) Arredondo, V. M.; McDonald, F. E.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 4871–4872.
(41) Arredondo, V. M.; Tian, S.; McDonald, F. E.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3633–3639.
(42) Collin, J.; Daran, J.-C.; Jacquet, O.; Schulz, E.; Trifonov, A. *Chem.−Eur. J.* **2005**, *11*, 3455–3462.
(43) Collin, J.; Daran, J.-C.; Schulz, E.; Trifonov, A. *Chem. Commun.* **2003**, 3048–3049.
(44) Gagne, M. R.; Brard, L.; Conticello, V. P.; Giardello, M. A.; Stern, C. L.; Marks, T. J. *Organometallics* **1992**, *11*, 2003–2005.
(45) Gribkov, D. V.; Hultzsch, K. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 5542–5546.
(46) Gribkov, D. V.; Hultzsch, K. C.; Hampel, F. *Chem.−Eur. J.* **2003**, *9*, 4796–4810.
(47) Heck, R.; Schulz, E.; Collin, J.; Carpentier, J.-F. *J. Mol. Catal. A: Chem.* **2007**, *268*, 163–168.
(48) Hong, S.; Marks, T. J. *J. Am. Chem. Soc.* **2002**, *124*, 7886–7887.
(49) Hong, S.; Tian, S.; Metz, M. V.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 14768–14783.
(50) Hultzsch, K. C.; Gribkov, D. V.; Hampel, F. *J. Organomet. Chem.* **2005**, *690*, 4441–4452.
(51) Ki, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 9295–9306.
(52) Lu, E.; Gan, W.; Chen, Y. *Organometallics* **2009**, *28*, 2318–2324.
(53) Molander, G. A.; Dowdy, E. D. *J. Org. Chem.* **1999**, *64*, 6515–6517.
(54) Molander, G. A.; Hasegawa, H. *Heterocycles* **2004**, *64*, 467–474.
(55) Motta, A.; Fragala, I. L.; Marks, T. J. *Organometallics* **2006**, *25*, 5533–5539.
(56) O'Shaughnessy, P. N.; Knight, P. D.; Morton, C.; Gillespie, K. M.; Scott, P. *Chem. Commun.* **2003**, 1770–1771.
(57) Panda, T. K.; Hrib, C. G.; Jones, P. G.; Jenter, J.; Roesky, P. W.; Tamm, M. *Eur. J. Inorg. Chem.* **2008**, 4270–4279.
(58) Panda, T. K.; Zulys, A.; Gamer, M. T.; Roesky, P. W. *J. Organomet. Chem.* **2005**, *690*, 5078–5089.
(59) Panda, T. K.; Zulys, A.; Gamer, M. T.; Roesky, P. W. *Organometallics* **2005**, *24*, 2197–2202.
(60) Riegert, D.; Collin, J.; Meddour, A.; Schulz, E.; Trifonov, A. *J. Org. Chem.* **2006**, *71*, 2514–2517.
(61) Ryu, J.-S.; Marks, T. J.; McDonald, F. E. *Org. Lett.* **2001**, *3*, 3091–3094.
(62) Tian, S.; Arredondo, V. M.; Stern, C. L.; Marks, T. J. *Organometallics* **1999**, *18*, 2568–2570.
(63) Wang, Q.; Xiang, L.; Song, H.; Zi, G. *J. Organomet. Chem.* **2009**, *694*, 691–696.
(64) Yu, X.; Marks, T. J. *Organometallics* **2007**, *26*, 365–376.
(65) Zi, G.; Wang, Q.; Xiang, L.; Song, H. *Dalton Trans.* **2008**, 5930–5944.
(66) Kim, H.; Livinghouse, T.; Shim, J. H.; Lee, S. G.; Lee, P. H. *Adv. Synth. Catal.* **2006**, *348*, 701–704.
(67) Kim, J. Y.; Livinghouse, T. *Org. Lett.* **2005**, *7*, 4391–4393.
(68) Kim, Y. K.; Livinghouse, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 3645–3647.
(69) Kim, Y. K.; Livinghouse, T.; Horino, Y. *J. Am. Chem. Soc.* **2003**, *125*, 9560–9561.
(70) Ackermann, L.; Bergman, R. G.; Loy, R. N. *J. Am. Chem. Soc.* **2003**, *125*, 11956–11963.
(71) Ackermann, L.; Sandmann, R.; Kaspar, L. T. *Org. Lett.* **2009**, *11*, 2031–2034.
(72) Cao, C.; Li, Y.; Shi, Y.; Odom, A. L. *Chem. Commun.* **2004**, 2002–2003.
(73) Heutling, A.; Pohlki, F.; Bytschkov, I.; Doye, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 2951–2954.
(74) Kaspar, L. T.; Fingerhut, B.; Ackermann, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 5972–5974.
(75) Li, C.; Thomson, R. K.; Gillon, B.; Patrick, B. O.; Schafer, L. L. *Chem. Commun.* **2003**, 2462–2463.
(76) Pohlki, F.; Doye, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 2305–2308.
(77) Tillack, A.; Castro, I. G.; Hartung, C. G.; Beller, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 2541–2543.
(78) Tillack, A.; Jiao, H.; Castro, I. G.; Hartung, C. G.; Beller, M. *Chem.−Eur. J.* **2004**, *10*, 2409–2420.
(79) Vujkovic, N.; Ward, B. D.; Maisse-Francois, A.; Wadepohl, H.; Mountford, P.; Gade, L. H. *Organometallics* **2007**, *26*, 5522–5534.
(80) Weitershaus, K.; Ward, B. D.; Kubiak, R.; Müller, C.; Wadepohl, H.; Doye, S.; Gade, L. H. *Dalton Trans.* **2009**, 4586–4602.
(81) Zhang, Z.; Leitch, D. C.; Lu, M.; Patrick, B. O.; Schafer, L. L. *Chem.−Eur. J.* **2007**, *13*, 2012–2022.
(82) Ackermann, L.; Kaspar, L. T.; Althammer, A. *Org. Biomol. Chem.* **2007**, *5*, 1975–1978.
(83) Kim, H.; Lee, P. H.; Livinghouse, T. *Chem. Commun.* **2005**, 5205–5207.
(84) Kim, H.; Livinghouse, T.; Lee, P. H. *Tetrahedron* **2008**, *64*, 2525–2529.
(85) Knight, P. D.; Munslow, I.; O'Shaughnessy, P. N.; Scott, P. *Chem. Commun.* **2004**, 894–895.
(86) Lee, A. V.; Schafer, L. L. *Organometallics* **2006**, *25*, 5249–5254.
(87) Smolensky, E.; Kapon, M.; Eisen, M. S. *Organometallics* **2007**, *26*, 4510–4527.
(88) Thomson, R. K.; Bexrud, J. A.; Schafer, L. L. *Organometallics* **2006**, *25*, 4069–4071.
(89) Watson, D. A.; Chiu, M.; Bergman, R. G. *Organometallics* **2006**, *25*, 4731–4733.
(90) Wood, M. C.; Leitch, D. C.; Yeung, C. S.; Kozak, J. A.; Schafer, L. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 354–358.
(91) Baudequin, C.; Brunet, J.-J.; Rodriguez-Zubiri, M. *Organometallics* **2007**, *26*, 5264–5266.
(92) Burling, S.; Field, L. D.; Messerle, B. A.; Turner, P. *Organometallics* **2004**, *23*, 1714–1721.
(93) Field, L. D.; Messerle, B. A.; Vuong, K. Q.; Turner, P. *Dalton Trans.* **2009**, 3599–3614.
(94) Field, L. D.; Messerle, B. A.; Vuong, K. Q.; Turner, P.; Failes, T. *Organometallics* **2007**, *26*, 2058–2069.
(95) Fukumoto, Y.; Asai, H.; Shimizu, M.; Chatani, N. *J. Am. Chem. Soc.* **2007**, *129*, 13792–13793.
(96) Liu, Z.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 1570–1571.
(97) Takemiya, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 6042–6043.
(98) Field, L. D.; Messerle, B. A.; Wren, S. L. *Organometallics* **2003**, *22*, 4393–4395.
(99) Lai, R.-Y.; Surekha, K.; Hayashi, A.; Ozawa, F.; Liu, Y.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **2007**, *26*, 1062–1068.
(100) Cochran, B. M.; Michael, F. E. *J. Am. Chem. Soc.* **2008**, *130*, 2786–2792.
(101) Li, K.; Hii, K. K. *Chem. Commun.* **2003**, 1132–1133.
(102) Lutete, L. M.; Kadota, I.; Yamamoto, Y. *J. Am. Chem. Soc.* **2004**, *126*, 1622–1623.
(103) Michael, F. E.; Cochran, B. M. *J. Am. Chem. Soc.* **2006**, *128*, 4246–4247.
(104) Qiu, S.; Wei, Y.; Liu, G. *Chem.−Eur. J.* **2009**, *15*, 2751–2754.
(105) Sakai, N.; Ridder, A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 8134–8135.
(106) Shaffer, A. R.; Schmidt, J. A. R. *Organometallics* **2008**, *27*, 1259–1266.
(107) Utsunomiya, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 14286–14287.

In our ongoing research on zinc-catalyzed hydroamination we also described the preparation of zinc complexes with sterically and electronically modified ATI ligands and studied the influence of structural modifications on their catalytic activity.[129,130] In this context we first investigated the influence of steric modifications of the substituents R of the $\{(R)_2ATI\}^-$ systems.[129,130] We were able to show the major influence of the steric environment around the zinc atom on both reactivity and stability of the corresponding complexes. Complexes bearing ligands with cyclic alkyl groups, especially cyclohexyl, showed superior activity in a number of selected reactions with functionalized aminoalkenes. In a second project we aimed to increase the activity of aminotroponiminate zinc complexes by changing the electronic properties of the ligand. We could demonstrate that the electronically modified zinc complex 5-phenylsulfanyl-*N*-isopropyl-2-(isopropylamino)troponiminate zinc methyl, [{PhS-ATI(*i*Pr)$_2$}ZnMe], has an increased reactivity in the intramolecular hydroamination reaction of non-activated alkenes compared to the parent, nonsubstituted complex.[131]

Motivated by these preliminary findings, we were interested in a broader study of the effect of the electronic properties of the aminotroponiminate ligand on the zinc-catalyzed intramolecular hydroamination reaction in more detail. Hence, we herein describe the synthesis and characterization of 10 aminotroponiminate zinc methyl complexes, [{R-ATI(*i*Pr)$_2$}ZnMe], bearing different substituents in the 5-position of the ligand. The new complexes were studied as precatalysts for the intramolecular hydroamination reaction in terms of their activity and stability. We were also interested to learn if a combination of steric modifications of the alkyl groups R of the $\{(R)_2ATI\}^-$ systems and electronic modifications in the 5-position has an additive effect.

Experimental Section

General Procedures. 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 glovebox. Tetrahydrofuran was predried over 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 (all ≥99 atom % D) or Euriso-Top GmbH (all ≥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 or on a Bruker DRX 500 spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Mass spectra were recorded at 70 eV on a Varian MAT 711. IR spectra were obtained on a Shimadzu FTIR-8400s or on a Nicolet FT-IR 750 spectrometer. Elemental analyses were carried out with an Elementar Vario EL III. $[PhNMe_2H][B(C_6F_5)_4]$ was purchased from Strem. $ZnMe_2$ was obtained from Sigma-Aldrich. (1-Allylcyclohexylmethyl)benzylamine,[109] benzyl-(2,2-diphenylpent-4-enyl)-amine,[109] (2,2-diphenylpent-4-enyl)furan-2-ylmethylamine,[130] (2,2-diphenylpent-4-enyl)thiophen-2-ylmethylamine,[130] H-ATI-(*i*Pr)$_2$H,[132] (4-bromo-7-isopropyliminocyclohepta-1,3,5-trienyl)isopropylamine, {Br-ATI(*i*Pr)$_2$}H, (**1a**),[131] isopropyl-(7-isopropylimino-4-phenylsulfanylcyclohepta-1,3,5-trienyl)amine (**5a**),[131] [{*N*-isopropyl-2-(isopropylamino)-5-phenylsulfanyltroponiminato}-methylzinc] (**5b**),[131] and *N*-cyclohexyl-2-(cyclohexylamino)-troponimine[129] were prepared according to literature procedures. The synthesis of compounds **2a**−**10a** is described in the Supporting Information.

General Procedure for the Synthesis of Complexes 1b−10b. A solution of the respective aminotroponimine in toluene was slowly added to an excess solution of $ZnMe_2$ in toluene at 0 °C. The solution was slowly warmed to room temperature and stirred for another 3 h. Then, the solution was filtered. After evaporating the solvents the residue was washed with *n*-pentane (2 × 5 mL).

5-Bromo-*N*-isopropyl-2-(isopropylamino)troponiminate Zinc Methyl (1b). A solution of **1a** (0.50 g, 1.77 mmol) in 25 mL of toluene was slowly added to a solution of $ZnMe_2$ (2.0 M in toluene, 2 mL, 4.0 mmol) in 15 mL of toluene. Yield: 0.35 g (55%). ^{1}H NMR (C_6D_6, 400 MHz): δ (ppm) −0.04 (s, 3 H), 1.06 (d, J = 6.3 Hz, 12 H), 3.58 (sept, J = 6.3 Hz, 2 H), 6.11 (d, J = 13.4 Hz, 2 H), 7.19 (t, J = 12.3 Hz, 2 H). ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ (ppm) −9.7, 24.0, 48.2, 109.9, 110.3, 136.4, 158.9. MS (EI, 80 eV): m/z (%) 362 [M^+] (58), 347 (83), 267 (69), 186 (50), 145 (100). Anal. Calcd for $C_{14}H_{21}N_2BrZn$ C: 46.37, H: 5.84, N: 7.73. Found: C: 46.48, H: 5.89, N: 7.53.

5-Iodo-*N*-isopropyl-2-(isopropylamino)troponiminate Zinc Methyl (2b). A solution of **2a** (0.10 g, 0.3 mmol) in 5 mL of toluene was slowly added to a solution of $ZnMe_2$ (1.2 M in toluene, 0.3 mL, 4.0 mmol) in 5 mL of toluene. Yield: 0.09 g (74%). ^{1}H NMR (C_6D_6, 400 MHz): δ (ppm) −0.04 (s, 3 H), 1.05 (d, J = 6.3 Hz, 12 H), 3.55 (sept, J = 6.3 Hz, 2 H), 5.95 (d, J = 12.1 Hz, 2 H), 7.36

(108) Bender, C. F.; Hudson, W. B.; Widenhoefer, R. A. *Organometallics* **2008**, *27*, 2356–2358.
(109) Bender, C. F.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 1070–1071.
(110) Brunet, J.-J.; Chu, N. C.; Diallo, O. *Organometallics* **2005**, *24*, 3104–3110.
(111) Brunet, J.-J.; Chu, N.-C.; Rodriguez-Zubiri, M. *Eur. J. Inorg. Chem.* **2007**, 4711–4722.
(112) Karshtedt, D.; Bell, A. T.; Tilley, T. D. *J. Am. Chem. Soc.* **2005**, *127*, 12640–12646.
(113) Reithofer, M. R.; Galanski, M.; Arion, V. B.; Keppler, B. K. *Chem. Commun.* **2008**, 1091–1093.
(114) Castonguay, A.; Spasyuk, D. M.; Madern, N.; Beauchamp, A. L.; Zargarian, D. *Organometallics* **2009**, *28*, 2134–2141.
(115) Fadini, L.; Togni, A. *Chem. Commun.* **2003**, 30–31.
(116) Fadini, L.; Togni, A. *Tetrahedron: Asymmetry* **2008**, *19*, 2555–2562.
(117) Ackermann, L.; Barfüsser, S.; Potukuchi, H. K. *Adv. Synth. Catal.* **2009**, *351*, 1064–1072.
(118) Munro-Leighton, C.; Delp, S. A.; Blue, E. D.; Gunnoe, T. B. *Organometallics* **2007**, *26*, 1483–1493.
(119) Ohmiya, H.; Moriya, T.; Sawamura, M. *Org. Lett.* **2009**, *11*, 2145–2147.
(120) Taylor, J. G.; Whittall, N.; Hii, K. K. *Org. Lett.* **2006**, *8*, 3561–3564.
(121) Zhou, L.; Bohle, D. S.; Jiang, H.-F.; Li, C.-J. *Synlett* **2009**, 937–940.
(122) Robinson, R. S.; Dovey, M. C.; Gravestock, D. *Tetrahedron Lett.* **2004**, *45*, 6787–6789.
(123) Kang, J.-E.; Kim, H.-B.; Lee, J.-W.; Shin, S. *Org. Lett.* **2006**, *8*, 3537–3540.
(124) Nishina, N.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 3314–3317.
(125) Nishina, N.; Yamamoto, Y. *Synlett* **2007**, 1767–1770.
(126) Zhang, J.; Yang, C.-G.; He, C. *J. Am. Chem. Soc.* **2006**, *128*, 1798–1799.
(127) Zhang, Y.; Donahue, J. P.; Li, C.-J. *Org. Lett.* **2007**, *9*, 627–630.
(128) Zhang, Z.; Lee, S. D.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2009**, *131*, 5372–5373.
(129) Dochnahl, M.; Löhnwitz, K.; Pissarek, J.-W.; Biyikal, M.; Schulz, S. R.; Schön, S.; Meyer, N.; Roesky, P. W.; Blechert, S. *Chem.−Eur. J.* **2007**, *13*, 6654–6666.
(130) Dochnahl, M.; Pissarek, J.-W.; Blechert, S.; Löhnwitz, K.; Roesky, P. W. *Chem. Commun.* **2006**, 3405–3407.
(131) Dochnahl, M.; Löhnwitz, K.; Pissarek, J.-W.; Roesky, P. W.; Blechert, S. *Dalton Trans.* **2008**, 2844–2848.
(132) Dias, H. V. R.; Jin, W.; Ratcliff, R. E. *Inorg. Chem.* **1995**, *34*, 6100–6105.

(d, J = 12.2 Hz, 2 H). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) −9.9, 24.0, 48.2, 111.34, 128.1, 142.52, 159.3. Anal. Calcd for $C_{14}H_{21}N_2IZn$ C: 41.05; H: 5.17; N: 6.84. Found C: 41.10; H: 5.56; N: 6.92.

5-Phenylazo-*N*-isopropyl-2-(isopropylamino)troponiminate Zinc Methyl (3b). A solution of **3a** (0.12 g, 0.4 mmol) in 5 mL of toluene was slowly added to a solution of $ZnMe_2$ (1.2 M in toluene, 0.5 mL, 0.6 mmol) in 5 mL of toluene. Yield: 0.15 g (99%). ^1H NMR (C_6D_6, 400 MHz): δ (ppm) −0.06 (s, 3 H), 1.04 (d, J = 6.2 Hz, 12 H), 3.67 (sept, J = 6.3 Hz, 2 H), 6.54 (d, J = 12.2 Hz, 2 H), 7.12 (d, J = 7.4 Hz, 1 H), 7.28 (t, J = 7.8 Hz, 2 H), 8.18 (d, J = 7.6 Hz, 2 H), 8.25 (d, J = 12.1 Hz, 2 H). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) −10.0, 23.9, 48.4, 109.9, 122.6, 129.1, 129.2, 131.0, 144.3, 153.6, 159.9. MS (EI, 80 eV): m/z (%) 386 [M^+] (100), 371 (73), 307 (26), 291 (76), 281 (40). HRMS $C_{20}H_{26}N_4Zn$: calcd 386.14490, found 386.14516.

5-Nitro-*N*-isopropyl-2-(isopropylamino)troponiminate Zinc Methyl (4b). A solution of **4a** (0.25 g, 1.0 mmol) in 10 mL of toluene was slowly added to a solution of $ZnMe_2$ (1.2 M in toluene, 1.0 mL, 1.2 mmol) in 10 mL of toluene. Yield: 0.20 g (61%). ^1H NMR (C_6D_6, 400 MHz): δ (ppm) −0.02 (s, 3 H), 1.07 (d, J = 6.3 Hz, 12 H), 3.59 (sept, J = 6.1 Hz, 2 H), 6.00 (d, J = 12.6 Hz, 2 H), 8.21 (d, J = 12.5 Hz, 2 H). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) −9.6, 23.7, 49.3, 107.3, 130.2, 136.4, 160.9. MS (EI, 80 eV): m/z (%) 327 [M^+] (100), 311 (57), 269 (11), 172 (26), 144 (34). HRMS $C_{14}H_{21}N_3O_2Zn$: calcd 327.09253, found 327.09186.

5-Phenylselenyl-*N*-isopropyl-2-(isopropylamino)troponiminate Zinc Methyl (6b). A solution of **6a** (0.20 g, 0.7 mmol) in 10 mL of toluene was slowly added to a solution of $ZnMe_2$ (1.2 M in toluene, 0.6 mL, 0.7 mmol) in 10 mL of toluene. Yield: 0.21 g (85%). ^1H NMR (C_6D_6, 400 MHz): δ (ppm) −0.03 (s, 3 H), 1.07 (d, J = 6.3 Hz, 12 H), 3.63 (sept, J = 6.3 Hz, 2 H), 6.28 (d, J = 11.8 Hz, 2 H), 6.91 (d, J = 5.7 Hz, 1 H), 6.97 (t, J = 7.6 Hz, 2 H), 7.45 (d, J = 7.1 Hz, 2 H), 7.54 (d, J = 12.1 Hz, 2 H). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) −10.0, 24.3, 48.4, 111.0, 116.3, 126.3, 127.8, 128.2, 129.5, 130.5, 142.4, 159.9. Anal. Calcd for $C_{20}H_{26}N_2SeZn$: C: 54.75; H: 5.97; N: 6.38. Found: C: 54.40; H: 6.10; N: 6.30.

5-Phenyltellanyl-*N*-isopropyl-2-(isopropylamino)troponiminate Zinc Methyl (7b). A solution of **7a** (0.35 g, 0.7 mmol) in 10 mL of toluene was slowly added to a solution of $ZnMe_2$ (1.2 M in toluene, 1.5 mL, 1.8 mmol) in 5 mL of toluene. Yield: 0.30 g (73%). ^1H NMR (d_8-THF 400 MHz): δ (ppm) −0.67 (s, 3 H), 1.24 (d, J = 6.3 Hz, 12 H), 3.99 (sept, J = 6.2 Hz, 2 H), 6.27 (d, J = 11.7 Hz, 2 H), 7.10 (m, 3 H), 7.51 (m, 2 H), 7.58 (d, J = 11.8 Hz, 2 H). $^{13}C\{^1H\}$ NMR (d_8-thf, 100 MHz): δ (ppm) −11.6, 24.2, 49.4, 97.5, 110.8, 119.0, 127.4, 129.9, 136.2, 147.8, 161.0. MS (EI, 80 eV): m/z (%) 487 [M^+] (54), 473 (29), 367 (47), 316 (21), 207 (38), 91 (100). Anal. Calcd for $C_{20}H_{26}N_2TeZn$: C: 49.28; H: 5.38; N: 5.75. Found: C: 49.00; H: 5.58; N: 5.45.

5-(3,5-Bis(trifluoromethyl)phenylsulfanyl)-*N*-isopropyl-2-(isopropylamino)troponiminate Zinc Methyl (8b). A solution of **8a** (0.10 g, 0.7 mmol) in 5 mL of toluene was slowly added to a solution of $ZnMe_2$ (1.2 M in toluene, 1.0 mL, 1.2 mmol) in 5 mL of toluene. Yield: 0.34 g (96%). ^1H NMR (C_6D_6, 400 MHz): δ (ppm) −0.06 (s, 3 H), 1.18 (d, J = 6.3 Hz, 12 H), 3.70 (sept, J = 6.7 Hz, 2 H), 6.29 (d, J = 11.9 Hz, 2 H), 7.28 (d, J = 7.3 Hz, 2 H), 7.42 (s, 1 H), 7.61 (s, 2 H). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) −10.0, 23.8, 48.4, 110.4, 113.9, 125.4, 127.6, 128.1, 132.3, 141.5, 146.0, 160.0. MS (EI, 80 eV): m/z (%) 526 [M^+] (16), 448 (36), 433 (35), 405 (100), 389 (42). HRMS $C_{22}H_{24}N_2F_6SZn$: calcd 526.08557, found 526.08490.

5-Benzenesulfinyl-*N*-isopropyl-2-(isopropylamino)troponiminate Zinc Methyl (9b). A solution of **9a** (0.24 g, 0.7 mmol) in 10 mL of toluene was slowly added to a solution of $ZnMe_2$ (1.2 M in toluene, 1.0 mL, 1.2 mmol) in 5 mL of toluene. Yield: 0.29 g (98%). ^1H NMR (C_6D_6, 400 MHz): δ (ppm) 0.20 (s, 3 H), 1.40 (d, J = 6.2 Hz, 6 H), 1.45 (d, J = 6.2 Hz, 6 H), 3.78 (sept, J = 6.5 Hz, 2 H), 5.96 (d, J = 12.0 Hz, 2 H), 6.93 (t, J = 7.3 Hz, 1 H), 7.01 (m, J = 7.9 Hz, 2 H), 7.15 (d, J = 7.2 Hz, 2H), 7.35 (d, J = 7.2 Hz, 2 H). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) −10.5, 23.9, 49.3, 108.4, 125.0, 127.3, 127.8, 190.0, 130.0, 160.2, 180.8. MS (EI, 80 eV): m/z (%) 406 [M^+] (64), 391 (18), 358 (26), 343 (32), 328 (100). HRMS $C_{20}H_{26}N_2OSZn$: calcd 406.10573, found 406.10514. Anal. Calcd for $C_{20}H_{26}N_2OSZn$: C: 58.89; H: 6.42; N: 6.87. Found: C: 58.48; H: 6.55; N: 6.60.

5-Phenylsulfanyl-*N*-cyclohexyl-2-(cyclohexylamino)troponiminate Zinc Methyl (10b). A solution of **10a** (0.36 g, 0.9 mmol) in 10 mL of toluene was slowly added to a solution of $ZnMe_2$ (1.2 M in toluene, 1.0 mL, 1.2 mmol) in 10 mL of toluene. Yield: 0.26 g (61%). ^1H NMR (C_6D_6, 400 MHz): δ (ppm) 0.04 (s, 3 H), 1.11 (m, 6 H), 1.39 (m, 4 H), 1.54 (d, J = 13.2 Hz, 2 H), 1.62 (m, J = 13.1 Hz, 4 H), 1.79 (d, J = 11.2 Hz, 4 H), 3.41 (m, 2 H), 6.48 (d, J = 12.1 Hz, 2 H), 6.88 (t, J = 7.4 Hz, 1 H), 7.02 (t, J = 7.4 Hz, 2 H), 7.33 (d, J = 7.3 Hz, 2 H), 7.42 (d, J = 12.1 Hz, 2 H). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ (ppm) −9.8, 25.8, 26.1, 35.2, 57.4, 110.9, 125.4, 127.0, 127.5, 129.2, 130.7, 141.6, 160.0. MS (EI, 80 eV): m/z (%) 470 [M^+] (100), 455 (10), 392 (11), 238 (21). HRMS $C_{26}H_{34}N_2SZn$: calcd 470.1734, found 470.1742.

General Procedure for the Intramolecular Hydroamination of Aminoalkenes on an NMR Tube Scale. A predried NMR tube was charged with the aminoalkene (430 μmol). A solution of the catalyst (11 μmol, 2.5 mol %) and $[PhNMe_2H][B(C_6F_5)_4]$ (9 mg, 11 μmol, 2.5 mol %) in 0.5 mL of C_6D_6 was added under a nitrogen atmosphere. The NMR tube was flame-sealed under vacuum. The reaction mixture was then heated to 80 °C for the stated duration of time. The reaction progress was monitored by ^1H NMR. When the reaction was judged to be complete, the crude reaction mixture was directly subjected to column chromatography on silica. All products were analyzed by ^1H and ^{13}C NMR, IR, MS, and HR-MS. The NMR yields were determined by comparing the integration of a well-resolved signal for the starting material with a well-resolved signal for the heterocyclic product. Ferrocene was used as internal standard for selected reactions (see Table 2).

X-ray Crystallographic Studies of 1b, 2b, 6b, and 10b. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the −73 °C cold stream of a STOE IPDS 2T diffractometer. Subsequent computations were carried out on an Intel Pentium Core2Duo PC.

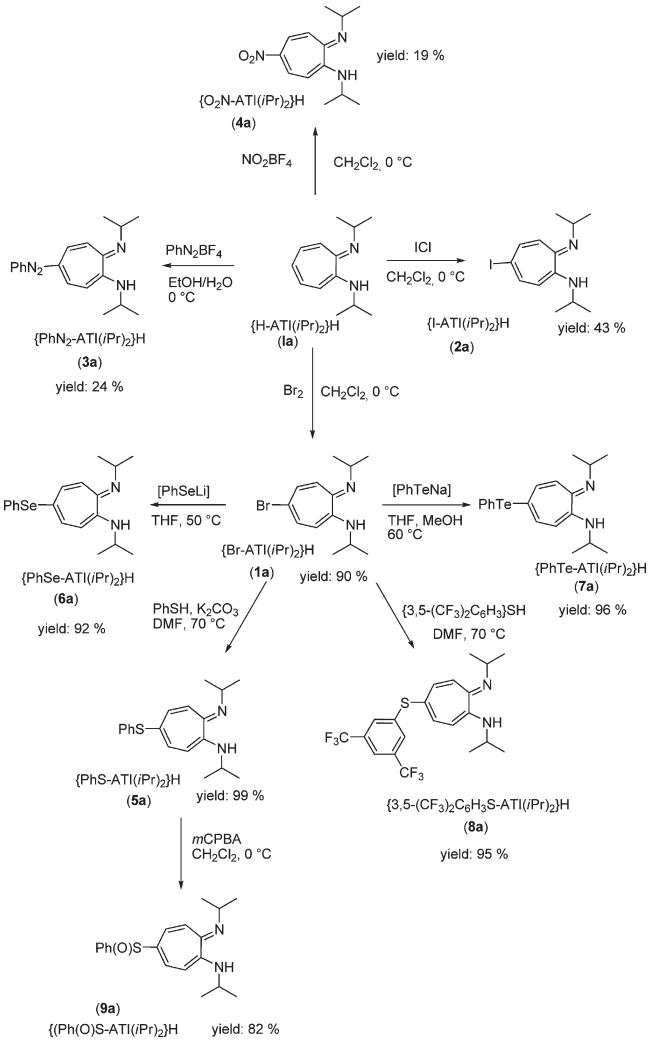
All structures were solved by the Patterson method (SHELXS-97[133]). The remaining non-hydrogen atoms were located from successive differences in Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $(F_o - F_c)^2$, where 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.[133] Carbon-bound hydrogen atom positions were calculated. The hydrogen atom contributions were calculated, but not refined. The final values of refinement parameters are given in the Supporting Information. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters, thermal parameters, and bond distances and angles have been deposited as Supporting Information.

Results and Discussion

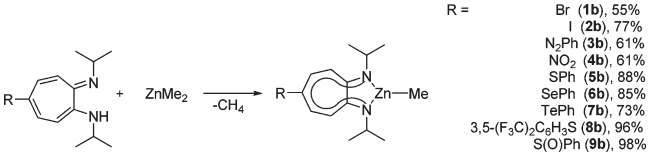
Ligand Synthesis A. Tropolone and aminotroponimine are electron-rich systems, which can undergo electrophilic aromatic substitution reactions.[134,135] Whereas the reaction of tropolone was reported to be unselective toward a bromination reaction,[136] early literature reports suggest that the

(133) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
(134) Sainsbury, M. In *Aromatic Chemistry*; Oxford University Press: Oxford, 1992.
(135) Taylor, R. J. K. In *Electrophilic Aromatic Substitution*; Wiley: Chichester, 1990.
(136) Pauson, P. L. *Chem. Rev.* **1955**, *55*, 9–136.

Scheme 2



Scheme 3



same type of reaction with aminotroponimine should be much more selective.[1,2] Halogenated aminotroponimines then can be further reacted with nucleophiles to form other derivatives.[1] Since we aimed to increase the activity of aminotroponiminate zinc complexes by changing the electronic properties of the ligand, we used *N*-isopropyl-2-(isopropylamino)troponimine, {H-ATI(*i*Pr)$_2$}H, as starting material to have later the possibility to compare the new system with the first-generation catalyst [H-ATI(*i*Pr)$_2$ZnMe] (**I**).[6] At a later stage of the project, we synthesized an additional aminotroponimine ligand with *N*-cyclohexyl groups because we were also interested to learn if a combination of steric modifications of the alkyl groups R in the {(R)$_2$ATI}$^-$ systems and electronic modifications in the 5-position has an additive effect.[129,130]

We previously reported that the reaction of {H-ATI(*i*Pr)$_2$}H with bromine at 0 °C selectively resulted in a bromination in the 5-position (Scheme 2).[131] The resulting product {Br-ATI(*i*Pr)$_2$}H (**1a**) was isolated in 90% yield. The reaction was

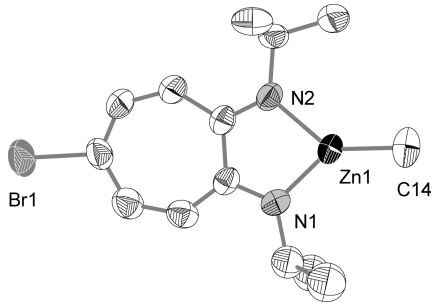


Figure 1. Perspective ORTEP view of the molecular structure of **1b**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity. Shown is one of the two independent molecules in the asymmetric unit. Selected distances [Å] and angles [deg]: N1−Zn 1.971(6), N2−Zn 1.977(5), Zn2−N3 1.967(6), Zn2−N4 1.974(6), Zn1−C14 1.941(7), Zn2−C28 1.932(7); N1−Zn−C14 139.6(3), N2−Zn−C14 138.9(3), N1−Zn−N2 81.4(2), N3−Zn2−C28 141.0(3), N4−Zn2−C28 137.8(3), N3−Zn2−N4 81.2(2).

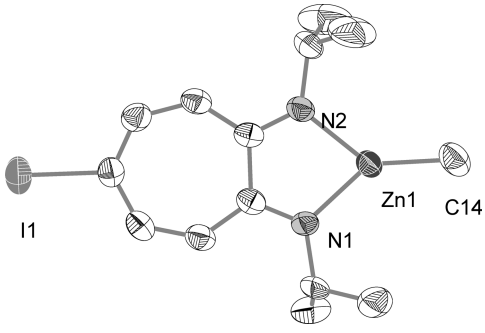


Figure 2. Perspective ORTEP view of the molecular structure of **2b**. Thermal ellipsoids are drawn to encompass 50% probability. Shown is one of the two independent molecules in the asymmetric unit. Selected bond lengths [Å] and angles [deg]: N1−Zn 1.971(2), N2−Zn 1.977(2), Zn2−N3 1.978(5), Zn2−N4 1.963(5), Zn−C14 1.953(3), Zn2−C28 1.943(6); N1−Zn−N2 82.57(9), N1−Zn−C14 139.37(10), N2−Zn−C14 137.35(10); N4−Zn2−C28 137.0(3), N3−Zn2−C28 140.9(3), N3−Zn2−N4 82.0(2).

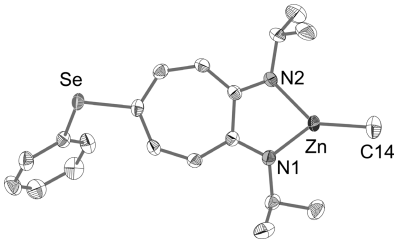
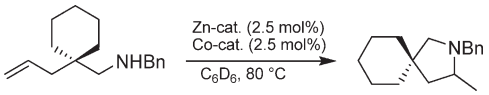


Figure 3. Perspective ORTEP view of the molecular structure of **6b**. Thermal ellipsoids are drawn to encompass 50% probability. Selected bond lengths [Å] and angles [deg]: N1−Zn 1.986(2), N2−Zn 1.992(2), Zn−C14 1.953(3); N1−Zn−N2 81.56(9), N1−Zn−C14 138.07(13), N2−Zn−C14 138.45(13).

performed at a scale of up to 30 mmol. In contrast, reactions with other electrophiles worked less smoothly. Thus, the reaction of {H-ATI(*i*Pr)$_2$}H with iodine monochloride gave the corresponding iodo species, {I-ATI(*i*Pr)$_2$}H (**2a**), in about 43% yield. The azo coupling of {H-ATI(*i*Pr)$_2$}H with

Table 1. Cyclization of (1-Allylcyclohexylmethyl)benzylamine[a]



entry	catalyst	time [h]	conv [%][b]	TOF [h^{-1}]
1	[{H-ATI(iPr)$_2$}ZnMe] (**I**)	0.5	quant.	80[129]
2	[{Br-ATI(iPr)$_2$}ZnMe] (**1b**)	0.75	quant.	53
3	[{I-ATI(iPr)$_2$}ZnMe] (**2b**)	10	59	2.4
4	[{PhN$_2$-ATI(iPr)$_2$}ZnMe] (**3b**)	10	93	3.7
5	[{NO$_2$-ATI(iPr)$_2$}ZnMe] (**4b**)	10	16	0.6
6	[{PhS-ATI(iPr)$_2$}ZnMe] (**5b**)	2	quant.	20[131]
7	[{PhSe-ATI(iPr)$_2$}ZnMe] (**6b**)	10	94	3.8
8	[{PhTe-ATI(iPr)$_2$}ZnMe] (**7b**)	10	97	3.9
9	[{(CF$_3$)$_2$C$_6$H$_3$S-ATI(iPr)$_2$}ZnMe] (**8b**)	10	95	3.8
10	[{PhS(O)-ATI(iPr)$_2$}ZnMe] (**9b**)	10	6	0.2

[a] Reaction conditions: 2.5 mol % of catalyst and 2.5 mol % of [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.

phenyl diazonium tetrafluoroborate[137] resulted in deep red {PhN$_2$-ATI(iPr)$_2$}H (**3a**) in 24% yield, and the reaction with NO$_2$BF$_4$[138] gave [NO$_2$-ATI(iPr)$_2$]H (**4a**) in 19% yield (Scheme 2). With respect to the yields all reactions were not optimized.

The subsequent nucleophilic aromatic substitution reactions were performed by treatment of the bromo compound **1a** with different nucleophiles. It has been reported before that the nucleophilic displacement with thiophenol in the presence of potassium carbonate in DMF proceeded smoothly and delivered the desired ligand {PhS-ATI(iPr)$_2$}H (**5a**) in quantitative yields from **1a**.[131] The analogous reactions with *in situ* generated PhSeH[139] and PhTeH[140] gave the corresponding species {PhSe-ATI(iPr)$_2$}H (**6a**) and {PhTe-ATI(iPr)$_2$}H (**7a**), respectively, in more than 90% yield. Obviously, the nucleophilic substitution reaction of **5a** effectively works with very soft nucleophiles. Thus, the reaction of **5a** with the soft nucleophile 3,5-bis(trifluormethyl)thiophenol resulted in {3,5-{(CF$_3$)$_2$C$_6$H$_3$S-ATI(iPr)$_2$}H (**8a**) in high yield, whereas no reaction with the harder nucleophile 2,4-dimethoxythiophenol was observed under the same conditions. To tune the donor strength of the substituent in the 5-position, we finally oxidized the sulfur atom of compound **5a**. Oxidation of **5a** with *m*CPBA in CH$_2$Cl$_2$ at 0 °C resulted in the sulfoxide {PhS(O)-ATI(iPr)$_2$}H (**9a**) in good yield (Scheme 2).

Attempts to replace the bromine atom with less-stabilized nucleophiles based on nitrogen and oxygen were all met with failure.

Metal Complexes A. The previously reported complexes [{H-ATI(iPr)$_2$}ZnMe] (**I**) and [{PhS-ATI(iPr)$_2$}ZnMe] (**5b**) were prepared by the reaction of {(iPr)$_2$ATI}H and [{PhS-ATI(iPr)$_2$}H, respectively, with ZnMe$_2$ in high yields.[131,141] In a similar synthetic procedure we reacted the neutral aminotroponimines {R-ATI(iPr)$_2$}H (**1a**−**4a** and **6a**−**9a**) with an excess of ZnMe$_2$ in toluene at 0 °C. All reactions were judged to be complete after the gas evolution had stopped, which was usually the case after three hours. Under these conditions the reaction exclusively led to the formation of methylzinc complexes of general composition [{R-ATI(iPr)$_2$}ZnMe] (R = Br (**1b**), I (**2b**), PhN$_2$ (**3b**), NO$_2$ (**4b**), PhSe (**6b**), PhTe (**7b**), 3,5-(CF$_3$)$_2$C$_6$H$_3$S (**8b**), PhS(O) (**9b**)) (Scheme 3).

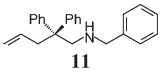
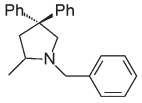
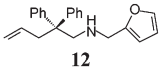
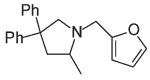
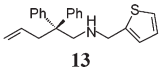
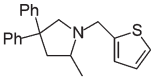
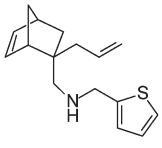
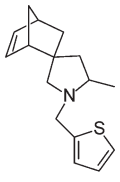
The ^{1}H and ^{13}C{^{1}H} NMR spectra of all compounds showed the expected set of signals. The chemical shift of the Zn-Me groups was observed for all compounds in a characteristic region. Thus, in the ^{1}H NMR this signal was seen around 0 ppm, whereas in the ^{13}C{^{1}H} NMR this signal was found between −9.6 and −10.0 ppm. This observation is in agreement with the chemical shifts observed for compound **I** (δ ^{1}H 0.00 ppm; ^{13}C{^{1}H} −9.89 ppm).[141] The EI mass spectra show the molecular ion peak [M$^+$] for all compounds whose MS data were acquired.

Furthermore, the structures of **1b**, **2b**, and **6b** were confirmed by single-crystal X-ray diffraction in the solid state (Figures 1−3). Data collection parameters and selected bond lengths and angles are given in Table 1 and in the captions of Figures 1−3. Compounds **1b** and **2b** are isostructural to each other. Both crystallize in the monoclinic space group $P2_1/c$ with two independent molecules of the corresponding zinc complex in the asymmetric unit. As observed for other aminotroponiminate zinc compounds, the metal atoms of all three complexes are coordinated in a trigonal-planar fashion. The Zn−N distances are between 1.967(6) and 1.992(2) Å, comparable to the previously published ATI zinc compounds.[6,129−131,142] The Zn−C distances are in the range 1.932(7) to 1.953(3) Å. These distances are typical for zinc methyl bonds.[6,129−131,142]

Catalysis A. The above synthesized complexes were used as precatalysts for the cyclization of (1-allylcyclohexylmethyl)-benzylamine in order to study the influence of the electronic modifications of compounds **1b**−**9b** on the hydroamination cyclization reaction. The reactions were performed under previously established conditions. All reactions were carried out in C$_6$D$_6$ at 80 °C with a low catalyst loading of 2.5 mol %. The reactions were conducted with one equivalent (with respect to the catalyst) of [PhNMe$_2$H][B(C$_5$F$_5$)$_4$] as a cocatalyst. The results of this screening, reaction times and yields, are shown in Table 1 and Figure 4. Obviously, the results obtained with the different complexes differ significantly, and the catalysts can be subdivided into different groups of reactivity.

(137) Dunker, M. F. W.; Starkey, E. B.; Jenkins, G. L. *J. Am. Chem. Soc.* **1936**, *58*, 2308–2309.
(138) Olah, G. A. *J. Org. Chem.* **2005**, *70*, 2413–2429.
(139) Gysling, H. J.; Luss, H. R. *Organometallics* **1989**, *8*, 363–368.
(140) Detty, M. R.; Murray, B. J.; Smith, D. L.; Zumbulyadis, N. *J. Am. Chem. Soc.* **1983**, *105*, 875–882.
(141) Herrmann, J.-S.; Luinstra, G. A.; Roesky, P. W. *J. Organomet. Chem.* **2004**, *689*, 2720–2725.
(142) Meyer, N.; Roesky, P. W. *Organometallics* **2009**, *28*, 306–311.

Table 2. Comparison of the Reactivity of the New Catalysts Established Systems[a]

entry	cat	Substrate	Time	Conv. /Yield[b]	Product
1	**I**		95 min[129]	quant.	
2	**II**		20 min[129]	quant. 90 %[c]	
3	**1b**	 **11**	17 h	97 %	
4	**5b**		40 min[131]	quant. 93 %[c]	
5	**6b**		8 h 26 h	80 % 97 %	
6	**10b**		27.5 h	96 %	
7	**I**		6 h	quant.	
8	**II**		2.5 h[129]	quant. 95 %[c]	
9	**1b**	 **12**	15 h	97 %[e]	
10	**5b**		4 h[131]	quant. 96 %[c]	
11	**6b**		13 h 21 h	94 % quant.	
12	**10b**		18 h	99 %	
13	**I**		20 min[130]	quant.[d]	
14	**II**		10 min[130]	quant.[d] 97 %[c]	
15	**1b**		4.5 h	quant.	
16	**5b**	 **13**	5 h	quant.[e]	
17	**6b**		6.5 h	97 %	
18	**10b**		8.5 h	quant.	
19	**I**		30 h[130]	93 %	
20	**II**	 **14**	2 h[130]	96 % 86 %[c]	
21	**5b**		2 h	98 % 96 %[c]	

[a] Reagents and conditions: substrate (430 μmol), catalyst (2.5 mol %), $[PhNMe_2H][B(C_6F_5)_4]$ (2.5 mol %), C_6D_6, 80 °C. [b] Determined by ^1H NMR. [c] Isolated yield. [d] The reaction was performed with 0.8 mol % $[PhNMe_2H][B(C_6F_5)_4]$. [e] The reaction was additionally performed with ferrocene as an internal standard.

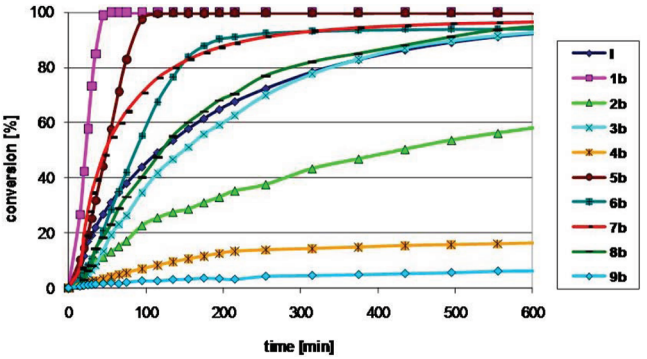


Figure 4. Cyclization of (1-allylcyclohexylmethyl)benzylamine using compounds **I** and **1b**−**9b**.

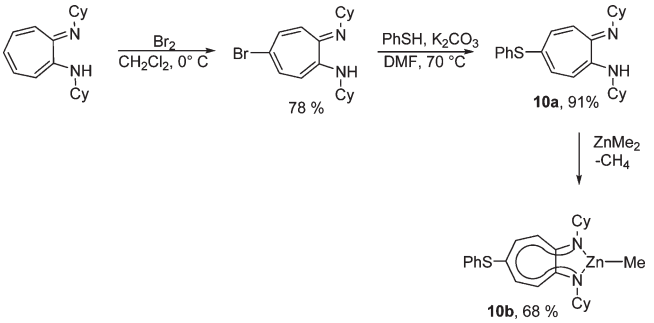
Using compounds **4b** and **9b** as catalysts (entries 5 and 10) resulted in very low conversions of less than 20%. The iodo-substituted complex gave about 60% conversion, whereas all other complexes catalyzed the reaction to at least 93% conversion to the desired product. The highest turnover frequencies (TOF) were observed with the first-generation catalysts **I** (entry 1) as well as with the bromo (**1b**, entry 2) and the phenylsulfanyl compounds (**5b**, entry 6). Interestingly the brominated compound **1b** showed a high initial activity. However, a detailed kinetic investigation revealed that this compound was very labile under the used reaction conditions, leading to a rapidly decreasing catalytic activity. Apparently some rapid decomposition of the catalyst took place. As a result of this decomposition process, the measured results in the catalysis tests lack sufficient reproducibility. To get more insight into the decomposition process, the reaction mixture with complex **1b** was analyzed after aqueous workup. It could be shown by NMR and MS that the bromine atom had been replaced by a hydrogen atom. Next the ligand precursor **1a** was heated with the amine **11** for 20 h at 120 °C. In contrast to earlier observations by Schafer et al. no reaction and thus no nucleophilic substitution by the substrate was oberserved.[143] Heating complex **1b** without $[PhNMe_2H][B(C_6F_5)_4]$ for 16 h at 80 °C did not result in any decomposition of the catalyst. Therefore we suggest that under catalytic conditions the active zinc species reacts in an intermolecular fashion with the bromine atom of the ligand.

These results led us to the following conclusions: (i) the substituent in the 5-position has a significant influence on the reaction rate. The effects are much greater than the influence of different groups at the nitrogen atoms of the aminotroponiminate ligands. (ii) The incorporation of electron acceptors such as nitro or sulfoxide groups in the 5-position decreased the activity of the corresponding zinc catalyst. This is most impressively seen by a comparison of compounds **5b** and **9b**. A simple oxidation of the sulfur atom has a dramatic influence on the activity. The TOF is decreased by about 2 orders of magnitude.

The low activity of catalysts bearing electron-accepting groups can be rationalized by the Lewis basic nature of these substituents. Accordingly, they may intermolecularly coordinate to the zinc atom of another complex and thus block the vacant coordination sites for incoming substrate molecules. To support this assumption, the catalytic conversion of substrate **11** with complex **I** as catalyst was repeated in the

(143) Bexrud, J. A.; Li, C.; Schafer, L. L. *Organometallics* **2007**, *26*, 6366–6372.

Scheme 4



presence of catalytic amounts of DMSO to mimic the sulfinyl group in compound **9b** and in the presence of catalytic amounts of nitrobenzene to mimic the nitro group in compound **4b**, respectively. No catalytic conversion was observed in the presence of DMSO, whereas in the presence of nitrobenzene a significantly lower reaction rate was observed.

The effects of the electron-donating substituents are less obvious. Electron-donating substituents increase the electron density of the ligand and thus decrease the Lewis acidity of the metal. We suggest that the numbers of substrate molecules, which are coordinated to the metal center, are thus decreased. It was shown earlier that in hydroamination cyclization catalysis the cyclization of the substrate is facilitated by a sterically less hindered metal center.[144,145] Thus, a low-coordinated zinc species should be more reactive than a higher coordinated one.

Ligand Synthesis and Metal Complex B. In the second stage of our investigation, we wanted to use aminotroponimines with other *N*-alkyl groups as starting material for the functionalization in the 5-position. Since we have shown that complexes with ligands bearing cyclohexyl groups at the nitrogen atoms showed superior activities in a number of selected reactions with functionalized aminoalkenes,[129,130] we used *N*-cyclohexyl-(2-cyclohexylamino)troponimine, {H-ATI(Cy)$_2$}H, as starting material. In a procedure analogous to the synthesis of compounds **1a** and **5a** the cyclohexyl derivatives 4-bromocyclohexyl-(7-cyclohexyliminocyclohepta-1,3,5-trienyl)amine, {Br-ATI(Cy)$_2$}H, and cyclohexyl-(7-cyclohexylimino-4-phenylsulfanylcyclohepta-1,3,5-trienyl)amine {PhS-ATI(Cy)$_2$}H (**10a**) were synthesized (Scheme 4). High yields were obtained in both steps (Scheme 4). The zinc compound [{PhS-ATI(Cy)$_2$}ZnMe] (**10b**) was obtained as a yellow crystalline, analytically pure solid, which was characterized by ^{1}H and ^{13}C NMR spectroscopy. The NMR spectra showed the expected set of signals with the characteristic low-field-shifted signal of the Zn-Me group and were observed for all compounds in a characteristic region (δ ^{1}H 0.04 ppm; ^{13}C{^{1}H} −9.8 ppm).

Furthermore, the structure of compound **10b** was confirmed by single-crystal X-ray diffraction in the solid state (Figures 5). Data collection parameters and selected bond lengths and angles are given in Table 1 and in the captions of Figure 5. Compound **5** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. As observed for other compounds **1b**, **2b**, and **6b**, the zinc atom is coordinated in a trigonal-planar fashion showing Zn−N bond distances of N1−Zn 1.982(4) Å and N2−Zn 1.979(4) Å and a Zn−C bond distance of 1.935(5) Å.

(144) Gagne, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275–294.
(145) Tobisch, S. *J. Am. Chem. Soc.* **2005**, *127*, 11979–11988.

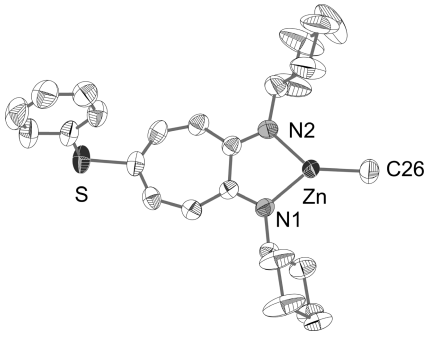


Figure 5. Perspective ORTEP view of the molecular structure of **10b**. Thermal ellipsoids are drawn to encompass 50% probability. Selected bond lengths [Å] and angles [deg]: N1−Zn 1.982(4), N2−Zn 1.979(4), Zn−C26 1.935(5); N1−Zn−N2 82.2(2), N1−Zn−C26 137.5(2), N2−Zn−C26 139.5(2).

Catalysis B. To have a better understanding of the different influences of both steric and electronic modifications of substituents attached to the aminotroponimine on the catalytic activity of the corresponding zinc complex in the intramolecular hydroamination reaction of non-activated terminal aminoolefins, we screened different classes of compounds (Table 2). As reference systems we used the first-generation catalyst **I** and the cyclohexyl complex [*N*-cyclohexyl-2-(cyclohexylamino)troponiminato] zinc methyl, [{(Cy)$_2$ATI}-ZnMe] (**II**), which was reported earlier to be a very active system. In addition we employed those compounds that had previously displayed the highest activities (see Table 1), i.e., compounds **1b**, **5b**, and **6b**. However, as already mentioned the application of **1b** is of limited use because of its rapid decomposition under the reaction conditions. Finally, we also tested compound **10b** as catalyst to study if a combination of steric and electronic modifications of the ligand had an additive effect. The results of this screening are shown in Table 2. The reactions were carried out at 80 °C in benzene-d_6 with a catalyst loading of 2.5 mol % and 2.5 mol % of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$]. Ferrocene was used as internal standard for selected examples. The isolated yields were around 90% or more in all the investigated cases. The reaction times greatly varied depending on both the substrate and the catalyst tested. As already mentioned, the bromine-substituted catalyst **1b** (entries 3, 9, and 15) decomposed rapidly. Thus, a significant amount of time was needed to reach quantitative conversions. The phenylsulfanyl complex **5b** (entries 4, 10, 16, and 21) was superior to the nonsubstituted first-generation catalyst **I** (entries 1, 7, 13, and 19) except for substrate **13**. The reactions with complexes **5b** and **II** (entries 2, 8, 14, and 20) showed that they displayed comparable activities for substrates **11**, **12**, and **14**. Replacement of the sulfur atom in compound **5b** by a selenium atom in compound **6b** had a detrimental effect on the catalytic activity (entries 5, 11, and 17), as the observed reaction times for compound **6b** are much higher. The logical combination of both modifications that had previously been shown to be beneficial, i.e., a phenylsulfanyl at the 5-position and cyclohexyl substituents at the nitrogen atoms, was realized in compound **10b**. The observed catalytic results (entries 6, 12, and 18) did not serve as a proof-of-concept for such additive effects. Instead of the expected decrease of the reaction times compared to the first-generation catalysts **I** (entries 1, 7, 13, and 19), a significant increase was observed. Obviously each effect, the increase of steric bulk of the ligand and the

increase of electron density of the metal center, separately increases the activity of the catalysts. We suggest that each effect lowers the coordination number on the zinc atom and thus facilitates the cyclization reaction, but no additive effects were observed.

Summary

In summary, we have prepared 10 substituted aminotroponimines that have different functional groups in the 5-position. We studied the complexation of these compounds to zinc and investigated the catalytic activity of the corresponding zinc complexes. We have demonstrated that electronic modifications of the ligand have a high impact on the catalytic activity of the zinc complexes. The attachment of electron-withdrawing groups such as nitro or sulfoxide groups in the 5-position significantly decreased the activity of the corresponding zinc catalyst. In contrast, donor substituents such as a thioether moiety at the backbone of the ligand, which increased the electron density at the nitrogen and the zinc atoms, also rendered the zinc atom more reactive. On the other hand, the brominated compound is very labile under the used catalytic conditions. Since it had previously been shown that zinc complexes bearing ATI ligands with cyclohexylamino groups gave superior activities in a number of selected reactions with functionalized aminoalkenes, we synthesized the corresponding complex bearing 5-phenylsulfanyl and cyclohexyl groups. An additional effect of both beneficial modifications on the catalytic activity of the zinc complexes was not observed. As an interpretation of these results, we suggest that each effect, the increase of the steric bulk of the ligand and the increase of electron density, lowers the coordination number of the zinc atom and thus increases the catalytic activity. On the other hand, it is not surprising that both effects do not sum up.

Acknowledgment. This work was supported by the Cluster of Excellence "Unifying Concepts in Catalysis" coordinated by the Technische Universität Berlin, by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Experimental details of the synthesis of compounds **2a**−**10a** and X-ray crystallographic files in CIF format for the structure determinations of **1b**, **2b**, **6b**, and **10b** are available free of charge via the Internet at http://pubs.acs.org.