Aminotroponate Zinc Complexes as Catalysts for the Intramolecular Hydroamination of Alkenes and Alkynes

Nils Meyer,[†] Karolin Löhnwitz,[†] Agustino Zulys,[†] Peter W. Roesky,*[,†] Maximilian Dochnahl,[‡] and Siegfried Blechert*[,‡]

Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstrasse 34-36, 14195 Berlin, Germany, and Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin, Germany

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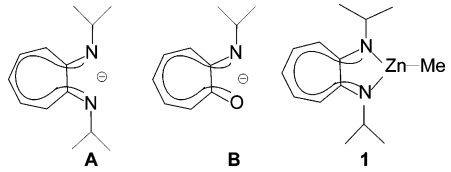
The dimeric complexes 2-(isopropylamino)troponate zinc methyl and ethyl $[(i\text{PrAT})\text{Zn-R}]_2$ (R = Me (**2a**), Et (**2b**)) were synthesized by reaction of (*i*PrAT)H with dimethyl and diethyl zinc, respectively, in toluene at low temperature. Reacting (*i*PrAT)H with dimethyl zinc at elevated temperature resulted in the double-substituted complex $[(i\text{PrAT})_2\text{Zn}]$ (**3**). Compounds **2a**,**b**, which were investigated by single-crystal X-ray diffraction, are dimeric in the solid state. The metal centers are bridged asymmetrically by two (μ)-oxygen atoms; thus a flat Zn−O−Zn′−O′ plane is observed. Compounds **2a**,**b** were used as the catalyst in the intramolecular hydroamination reaction of nonactivated terminal aminoolefins and one aminoalkyne. Good catalytic activities at elevated temperature were observed.

Introduction

Amines are typical intermediate products in the chemical industry, and their derivatives are of fundamental importance as natural products, pharmacological agents, fine chemicals, and dyes. Since today most amines are made in multistep syntheses, the hydroamination would offer the most attractive alternative synthetic route. Thus, there is considerable interest in the development of new synthetic protocols for the formation of carbon−nitrogen bonds. In this context, the direct addition of amine N−H bonds to C−C multiple bonds (hydroamination) is a particularly useful method.[1,2] It has been shown that hydroamination can be catalyzed by d- and f-block transition metals, by alkali metals,[3] and, very recently by calcium.[4] Early transition metals (group 4[2g,h] and especially the lanthanides[2k]) are highly efficient catalysts for the hydroamination reaction, but the high sensitivity of these catalysts toward moisture and air limits their synthetic application. Furthermore, they show a very limited tolerance to polar functional groups. On the other hand, late transition metal catalysts offer the advantage of greater polar functional group compatibility. However, most of these catalysts are based on the relatively expensive platinum metals[5] or on nickel,[6] which has only a limited use for the synthesis of pharmaceuticals. Moreover for nonactivated substrates most of the late transition metal catalysts show limited scope, modest selectivity, and sluggish reaction rates. In contrast, the application of zinc complexes as homogeneous catalysts for hydroamination is almost unknown. The application of zinc compounds is basically limited to zinc triflate[7,8] and supported catalysts.[9,10]

Scheme 1



Recently we reported the use of aminotroponiminate **A** as a ligand in organo zinc chemistry (Scheme 1). A new organozinc-based catalyst, *N*-isopropyl-2-(isopropylamino)troponiminate zinc methyl, [{(*i*Pr)$_2$ATI}Zn-Me] (**1**) (Scheme 1), was introduced for the hydroamination of nonactivated double and triple bonds.[11] Compound **1** is distinguished by a number of practical advantages such as the particular functional group tolerance (thioethers, amides, hydrazides, and hydroxylamines), good

* To whom correspondence should be addressed. E-mail: roesky@chemie.fu-berlin.de. Phone: +49 3083854004. Fax: +49 83852440.

† Freie Universität Berlin.

‡ Technische Universität Berlin.

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activity in the catalytic conversion of nonactivated C−C multiple bonds, and a relatively high stability toward moisture and air. It is also notable that access to seven-membered heterocycles was possible as well.

Motivated by these studies, we were interested in obtaining a better understanding of the influence of the ligand system of **1** on the catalytic activity. Therefore, we focused our interest on aminotroponate (**B**) alkyl complexes of zinc (Scheme 1). Formally, in aminotroponates the imine group is replaced by an oxo group. Thus, both ligand systems **A** and **B** are closely related. Whereas aminotroponate complexes of some main group[12] and transition metals[13,14] including zinc[14] are known, to the best of our knowledge no zinc alkyl complexes were reported so far.

Herein we report on the synthesis of 2-(isopropylamino)-troponate zinc methyl and ethyl [(*i*PrAT)Zn-R]$_2$ (R = Me, Et) and the application of these compounds as catalysts for the hydroamination reaction.

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 M. Braun glovebox. Ether solvents (tetrahydrofuran and ethyl ether) were predried over Na wire and distilled under nitrogen from K (THF) or Na wire (ethyl ether) benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft mbH (all ≥99 atom % D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded on a JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Raman spectra were performed on a Bruker RFS 100. Elemental analyses were carried out with an Elementar vario EL. 2-(*N*-Isopropylamino)tropone[15] was prepared according to literature procedures. $ZnMe_2$ and $ZnEt_2$ were purchased from Aldrich Inc.

[(*i*PrAT)ZnMe]$_2$ (2a). A 2 M solution of $ZnMe_2$ in toluene (1.6 mL, 3.1 mmol) was slowly added into a cooled solution (−32 °C) of (*i*PrAT)H (0.47 g, 2.9 mmol) in 10 mL of toluene. The solution was slowly warmed to room temperature, followed by gas evolution. The reaction mixture was stirred until the gas evolution stopped (1 h). The solution was evaporated, and the product was obtained analytically pure in nearly quantitative yield as a yellow powder. Yield: 0.68 g (1.4 mmol, 97%).

^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ −0.23 (s, 6 H, CH_3), 1.13 (d, 12 H, J(H,H) = 6.3 Hz, C*H*$(CH_3)_2$), 3.53 (sept., 2 H, J(H,H) = 6.2 Hz, C*H*$(CH_3)_2$), 6.15 (t, 2 H, J(H,H) = 8.8 Hz, CH_{ring}), 6.48 (d, 2 H, J(H,H) = 11.9 Hz, CH_{ring}), 6.58−6.67 (m, 4 H, CH_{ring}), 7.16 (d, 2 H, J(H,H) = 10.4 Hz, CH_{ring}). ^{13}C{^{1}H} NMR (C_6D_6, 100.4 MHz, 25 °C): δ −12.1 (CH_3), 23.4 (CH(*C*$H_3)_2$), 48.5 (*C*H-$(CH_3)_2$), 118.9 (C_{ring}), 119.3 (C_{ring}), 122.3 (C_{ring}), 135.7 (C_{ring}), 136.2 (C_{ring}), 162.9 (C_{ring}), 172.6 (C_{ring}). Anal. Calcd for $C_{22}H_{30}N_2O_2Zn_2$ (485.22): C, 54.45, H, 6.23, N, 5.77. Found: C, 54.35, H, 5.84, N, 5.69. Raman (solid [cm^{-1}]): 3059(w), 3022(w), 2970(m), 2929-(w), 2900(m), 2870(w), 1513(m), 1475(s), 1439(vs), 1277(s), 1221-(w), 1159(w), 958(w), 771(s), 544(w), 496(w), 295(s).

[(*i*PrAT)ZnEt]$_2$ (2b). Compound **2b** was prepared in the same way as **2a** using a 1 M solution of $ZnEt_2$ in hexane (6 mL, 6.0 mmol) and 0.93 g (5.7 mmol) of (*i*PrAT)H in 10 mL of toluene. X-ray quality crystals can be grown from a saturated ether solution at room temperature. The product was obtained in nearly quantitative yield as a yellow powder after evaporating the solvent. Yield: 1.44 g (2.8 mmol, 98%).

^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 0.69 (q, 4 H, J(H,H) = 7.7 Hz, C*H*$_2$CH$_3$), 1.02 (d, 12 H, J(H,H) = 6.2 Hz, C*H*$(CH_3)_2$), 1.56 (t, 6 H, J(H,H) = 7.7 Hz, CH$_2$C*H*$_3$), 3.40 (sept., 2 H, J(H,H) = 6.2 Hz, C*H*$(CH_3)_2$), 6.24 (t, 2 H, J(H,H) = 9.6 Hz, CH_{ring}), 6.16 (d, 2 H, J(H,H) = 12.1 Hz, CH_{ring}), 6.69−6.76 (m, 4 H, CH_{ring}), 7.19 (d, 2 H, J(H,H) = 10.4 Hz, CH_{ring}). ^{13}C{^{1}H} NMR (C_6D_6, 100.4 MHz, 25 °C): δ 3.2 (*C*H$_2$CH$_3$), 13.2 (CH$_2$*C*H$_3$), 23.5 (CH-(*C*$H_3)_2$), 48.0 (*C*H$(CH_3)_2$), 118.5 (C_{ring}), 120.2 (C_{ring}), 122.3 (C_{ring}), 136.0 (C_{ring}), 136.2 (C_{ring}), 163.0 (C_{ring}), 174.0 (C_{ring}). Raman (solid [cm^{-1}]): 3060(w), 3029(w), 2976(w), 2930(w), 2894(w), 1606-(w), 1573(w), 1512(m), 1437(s), 1437(vs), 1276(m), 978(w), 959-(w), 772(m), 495(m), 300(s). Anal. Calcd for $C_{24}H_{34}N_2O_2Zn_2$ (513.28): C, 56.16, H, 6.68, N, 5.46. Found: C, 55.69, H, 6.97, N, 5.40.

[(*i*PrAT)$_2$Zn] (3). A 2 M solution of $ZnMe_2$ in toluene (1.4 mL, 2.9 mmol) was slowly added into a solution of (*i*PrAT)H (0.93 g, 5.7 mmol) in 20 mL of toluene at room temperature and stirred for 2 h. After the gas evolution had stopped, the solution was heated to 65 °C for another 2 h and was then refluxed for 5 min. After evaporating the solvent the product was obtained as orange crystals from hot toluene. Yield: 1.82 g (2.4 mmol, 84%).

^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 1.07 (d, 12 H, J(H,H) = 6.2 Hz, C*H*$(CH_3)_2$), 3.54 (sept., 2 H, J(H,H) = 6.2 Hz, C*H*$(CH_3)_2$), 6.28 (t, 2 H, J(H,H) = 9.4 Hz, CH_{ring}), 6.57 (d, 2 H, J(H,H) = 11.8 Hz, CH_{ring}), 6.79−6.85 (m, 4 H, CH_{ring}), 7.30 (d, 2 H, J(H,H) = 10.8 Hz, CH_{ring}). ^{13}C{^{1}H} NMR (C_6D_6, 100.4 MHz, 25 °C): δ 23.8 (CH(*C*$H_3)_2$), 47.8 (*C*H$(CH_3)_2$), 116.6 (C_{ring}), 120.9 (C_{ring}), 121.0 (C_{ring}), 136.1 (C_{ring}), 137.0 (C_{ring}), 163.0 (C_{ring}), 176.7 (C_{ring}). MS (EI): *m*/*z* (%) = 388 ([M]$^+$, 46), 373 ([M − CH_3]$^+$, 100), 345 ([M − CH$(CH_3)_2$]$^+$, 31), 331 ([M − NCH$(CH_3)_2$]$^+$, 8), 226 ([M − *i*PrAT]$^+$, 5). Raman (solid [cm^{-1}]): 3054(w), 3029(w), 2989(w), 2931(w), 2905(w), 1618(m), 1510(s), 1470(s), 1430(vs), 1399(m), 1265(m), 1244(w), 983(m), 965(w), 857(w), 773(m), 497(s), 386-(s), 316(s). Anal. Calcd for $C_{20}H_{24}N_2O_2Zn_2$: C, 61.62, H, 6.21, N, 7.19. Found: C, 61.83, H, 6.24, N, 6.74.

General Procedure for the Hydroamination Reaction (NMR scale reaction). Compound **1** was weighed under argon gas into an NMR tube. C_6D_6 (∼0.7 mL) was condensed into the NMR tube. The reactant was injected onto the mixture, and the whole sample was mixed just before the insertion into the core of the NMR machine (t_0). Then the mixture was heated. The ratio between the reactant and the product was exactly calculated by comparison of the integration of the corresponding signals.

X-ray Crystallographic Studies of 2a,b. Crystals of **2a**,**b** were grown from saturated ether solutions. Suitable crystals were covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystals were transferred directly to the −73 °C cold N_2 stream of a Stoe IPDS 2T diffractometer. Subsequent computations were carried out on an Intel Pentium IV PC.

All structures were solved by the Patterson method (SHELXS-97[16]). The remaining non-hydrogen atoms were located from successive difference in Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on

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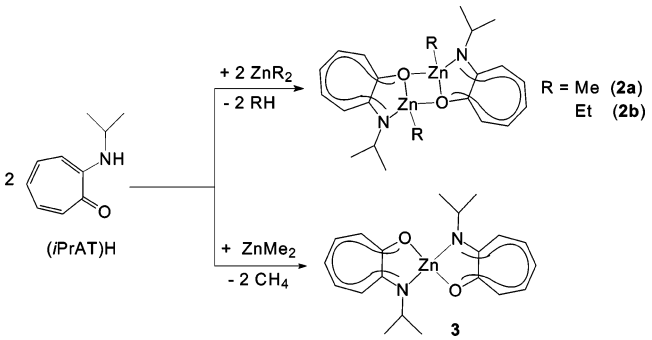
Scheme 2



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.[17] In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors. Carbon-bound hydrogen atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. The hydrogen atom contributions were calculated, but not refined. The final values of refinement parameters are given in Tables 1. 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. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-606948 (**2a**) and 606949 (**2b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

The Metal Complexes. The zinc alkyl complexes [(*i*PrAT)-Zn-R]$_2$ (R = Me (**2a**), Et (**2b**)) were obtained by reaction of the neutral ligand (*i*PrAT)H[15] with dimethyl and diethyl zinc, respectively, in toluene at low temperature (Scheme 2). Compounds **2a**,**b** were obtained as yellow crystalline powders showing almost no reactivity toward air and moisture. They were characterized by Raman and ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H and ^{13}C{^{1}H} NMR spectra show the expected set of signals for the (*i*PrAT)$^-$ ligand. The signals of the isopropyl C*H* of **2a**,**b** appear as well-resolved septets. The chemical shifts (δ 3.53 (**2a**) and 3.40 (**2b**) ppm) are in the range of **1** (δ 3.76).[11,18] In comparison to the starting materials $ZnMe_2$ (δ ^{1}H 0.51; ^{13}C{^{1}H} −4.2)[19] the signals of the Zn-Me group of **2a** (δ ^{1}H −0.23 ppm; ^{13}C{^{1}H} −12.1 ppm) are high field shifted, whereas no clear tendency is observed for the Zn-Et group (δ ^{1}H 0.69, 1.56 ppm; ^{13}C{^{1}H} 3.2, 13.2 ppm) in **2b** compared to $ZnEt_2$ (δ ^{1}H 0.08, 1.05;[20] ^{13}C{^{1}H} 6.82, 10.35).[21]

The structures of **2a**,**b** were confirmed by single-crystal X-ray diffraction in the solid state (Figures 1 and 2). Data collection parameters and selected bond lengths and angles are given in Tables 1 and 2. Compound **2a** crystallizes in the monoclinic space group $P2_1/n$ having two molecules in the unit cell, whereas compound **2b** crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the unit cell. The structures of compounds **2a**,**b** revealed a bridged structure in the solid state, which is in contrast to the monomeric compound **1**, where the zinc atom is 3-fold coordinated. The two [(*i*PrAT)Zn-R] units are connected via

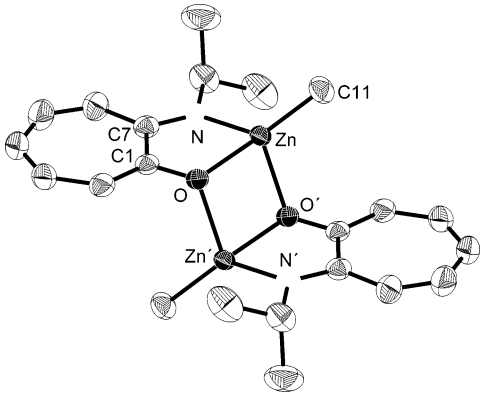


Figure 1. Perspective ORTEP view of the molecular structure of **2a**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity.

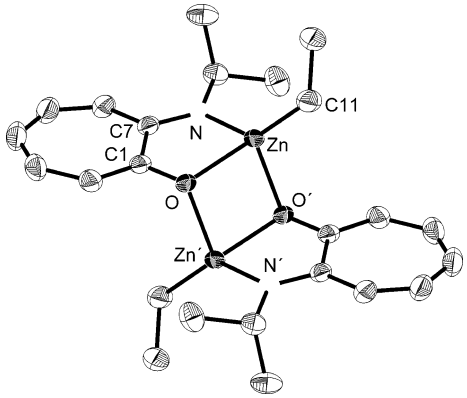


Figure 2. Perspective ORTEP view of the molecular structure of **2b**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity.

Table 1. Crystallographic Details of [(*i*PrAT)ZnMe]$_2$ (2a) and [(*i*PrAT)ZnEt]$_2$ (2b)[a]

	2a	**2b**
formula	$C_{22}H_{30}N_2O_2Zn_2$	$C_{24}H_{34}N_2O_2Zn_2$
fw	485.22	513.28
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	9.581(2)	8.2534(10)
b, Å	9.2854(14)	8.7691(11)
c, Å	12.740(3)	9.6387(13)
α, deg		77.741(10)
β, deg	91.95(2)	87.096(11)
γ, deg		61.936(9)
V, Å^3	1132.7(4)	600.56(13)
Z	2	1
density, g/cm^3	1.423	1.419
radiation	Mo Kα (*λ* = 0.71073 Å)	Mo Kα (*λ* = 0.71073 Å)
μ, mm^{-1}	2.136	2.018
abs corr	Integration (X-Shape)	Integration (X-Shape)
no. of reflns collected	8692	7608
no. of unique reflns	3045 [R_{int} = 0.0395]	3210 [R_{int} = 0.0235]
no. of obsd reflns	2546	2875
data; params	3045; 129	3210; 136
R1;[b] wR2[c]	0.0353; 0.0563	0.0257; 0.0619

[a] All data collected at 203 K. [b] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

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Table 2. Selected Bond Lengths and Angles of [(*i*PrAT)ZnMe]$_2$ (2a) and [(*i*PrAT)ZnEt]$_2$ (2b)

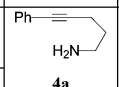
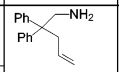
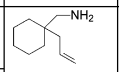
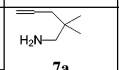
	2a	2b
	Bond Lengths (Å)	
Zn−N	1.994(2)	2.0059(13)
Zn−O	2.0493(15)	2.0542(11)
Zn−O′	2.1360(14)	2.1476(11)
Zn−C11	1.951(2)	1.9754(2)
Zn−Zn′	3.1283(8)	3.1182(6)
N−C7	1.336(3)	1.319(2)
O−C1	1.307(2)	1.318(2)
C1−C2	1.383(3)	1.380(2)
	Bond Angles (deg)	
N−Zn−O	79.39(7)	79.45(5)
N−Zn−O′	107.52(7)	103.72(5)
N−Zn−C11	129.57(9)	133.65(6)
O−Zn−O′	83.28(6)	84.20(5)
O−Zn−C11	133.43(10)	129.91(7)
O′−Zn−C11	112.69(9)	113.11(6)
Zn−O−Zn′	96.72(6)	95.80(5)
Zn−N1−C7	115.25(17)	114.97(10)
Zn−O−C1	113.98(13)	112.70(9)
Zn′−O−C1	116.54(11)	115.68(9)

two O bridges resulting in a flat Zn−O−Zn′−O′ ring. At the center of the Zn−O−Zn′−O′ plane, a crystallographic inversion center is observed. The Zn−Zn′ distance is 3.1283(8) Å in **2a** and 3.1182(6) Å in **2b**. The angles within the ring are O−Zn−O′ 83.28(6)° (**2a**), 84.20(5)° (**2b**) and Zn−O−Zn′ 96.72(6)° (**2a**), 95.80(5)° (**2b**). Thus, the metal centers are bridged asymmetrically by two μ-oxygen atoms having Zn−O distances of Zn−O 2.0493(15) Å (**2a**), 2.0542(11) Å (**2b**) and Zn−O′ 2.1360(14) Å (**2a**), 2.1476(11) Å (**2b**). The seven-membered carbon ring of the ligand, which is planar, is attached to the four-membered Zn−O−Zn′−O′ ring (e.g., N−Zn−O′ 107.52(7)° (**2a**) and 103.72(5)° (**2b**)). The four-coordinated zinc centers in **2a**,**b** exhibit a highly distorted tetrahedral geometry. The bond distances are in the expected range of Zn−C11 1.951(2) Å (**2a**), 1.9754(2) Å (**2b**) and Zn−N 1.994(2) Å (**2a**), 2.0059(13) Å (**2b**).

To further investigate the reactivity of (*i*PrAT)H, $ZnMe_2$ was reacted with 2 equiv of (*i*PrAT)H at elevated temperature to give the double-substituted complex [(*i*PrAT)$_2$Zn] (**3**) (Scheme 2). It has been shown earlier by us that the reaction of the related aminotroponimines with $ZnMe_2$ leads with dependence on the reaction temperature to either mono- or double-substituted products.[22] Compound **3** was characterized by MS, Raman, and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and elemental analysis. In the mass spectrum the molecular ion as well as its characteristic fragmentation pattern was observed. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **3** show the expected set of signals for the (*i*PrAT)$^-$ ligand. The chemical shifts of these signals are similar to those recorded for compounds **2a**,**b**. Thus, the signal of the isopropyl C*H* appears as a well-resolved septet having a chemical shift of δ 3.54 ppm.

Hydroamination Catalysis. Complexes **2a**,**b** were used as catalysts in the intramolecular hydroamination reaction of nonactivated terminal aminoolefins and one aminoalkyne (Table 3). Basically we were interested in comparing the activity of **2a**,**b** with **1** in order to improve the turnover frequencies. It turned out that aminoalkenes are converted to the products at 120 °C in high yield (entries 5−6, 8−9, 11−12). The aminoalkyne could even be reacted at 60 °C (entries 2−3). All of the reactions with aminoolefins and aminoalkynes proceed regiospecifically. Substrates bearing bulky geminal substituents

Table 3. Hydroamination Reaction of Terminal Aminoolefins and Alkynes[a]

Entry	Substrate	Product	Cat.	[Zn] [mol%][b]	Temp [°C]	Time [h]	Conversion [%][c]
1	 **4a**	 **4b**	**1**	5 10	60	58 10	Quant Quant
2			**2a**	5	60	67	Quant
3			**2b**	5	60	31	Quant
4	 **5a**	 **5b**	**1**	2 10	120 120	42 12	98 Quant[d]
5			**2a**	2	120	13	92
6			**2b**	2	120	13	Quant
7	 **6a**	 **6b**	**1**	5	120	28	Quant[d]
8			**2a**	10	120	72	Quant
9			**2b**	10 5	120	50 300	97 90
10	 **7a**	 **7b**	**1**	10	120	110	Quant
11			**2a**	10	120	90	Quant
12			**2b**	10	120	65	Quant

[a] 0.6 mmol of substrate; solvent: C_6D_6 in a *sealed* NMR tube. [b] Catalyst concentrations were calculated for the zinc atoms. [c] Determined by ^{1}H NMR. [d] Reference 11.

in the β-position with respect to the amino group (Thorpe−Ingold effect)[23] could be cyclized with reasonable catalyst loadings of 2−10 mol % with good to moderate reaction times. Substrate **5a** displayed the highest reactivity of the aminoolefins, giving the corresponding pyrrolidine within less than 15 h. It can be concluded from all reactions investigated so far that compound **2b** is slightly more reactive than **2a**. We suggest that the difference in reaction rate may be a result of different initial rates. A comparison of **1** with **2a**,**b** showed that the catalyst performance depended on the substrate. Thus, compound **6a** (entries 7−9) could be cyclized much faster by catalyst **1**. On the other hand substrate **5a** (entries 4−6) was converted about 3 times faster by **2b** compared to **1**. A similar but not significant tendency is observed for substrates **4a** (entry 1−3) and **7a** (entries 10−12), which are cyclized slightly faster by **2b** than by **1**.

Summary

In summary, we have prepared 2-(isopropylamino)troponate zinc methyl and ethyl [(*i*PrAT)Zn-R]$_2$ (R = Me (**2a**), Et (**2b**)) and the homoleptic double-substituted complex [(*i*PrAT)$_2$Zn] (**3**) by reaction of (*i*PrAT)H with ZnR_2. Complexes **2a**,**b** are as easily accessible as the corresponding aminotroponiminate complex **1**, and the catalytic activity for the hydroamination reaction is in most cases comparable but not significantly better. Considering the fact that almost nothing is known about the zinc-catalyzed hydroamination in homogeneous phase, we plan to test a number of different ligand systems to get a better understanding of the influence of the ligand for this reaction.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **2a**,**b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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