Organometallics **2008,** *27,* 1207–1213 1207

Aminotroponiminate Complexes of the Heavy Alkaline Earth and the Divalent Lanthanide Metals as Catalysts for the Hydroamination/Cyclization Reaction

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Received October 10, 2007

Reaction of SrI_2, $EuI_2(THF)_2$, and $YbI_2(THF)_2$ with $KN(SiMe_3)_2$ and $[\{(i\text{Pr})_2\text{ATI}\}\text{K}]$ ($(i\text{Pr})_2\text{ATI}$ = *N*-isopropyl-2-(isopropylamino)troponiminate) led to monoaminotroponiminate complexes of the heavier alkaline earth elements and the related divalent lanthanides of composition $[\{(i\text{Pr})_2\text{ATI}\}\text{M}\{\text{N}(\text{SiMe}_3)_2\}(\text{THF})_2]$ (M = Sr, Eu, Yb). Diaminotroponiminate complexes of composition $[\{(i\text{Pr})_2\text{ATI}\}_2\text{M}(\text{THF})_2)]$ (M = Sr, Ba) were obtained by the reaction of SrI_2 and BaI_2 with 2 equiv of $[\{(i\text{Pr})_2\text{ATI}\}\text{K}]$. All new compounds were characterized by single-crystal X-ray diffraction. Independent of the ionic radius of the center metal all monoaminotroponiminate complexes $[\{(i\text{Pr})_2\text{ATI}\}\text{M}\{\text{N}(\text{SiMe}_3)_2\}(\text{THF})_2]$ including the previously reported Ca analogue are isostructural. The same phenomenon is observed for $[\{(i\text{Pr})_2\text{ATI}\}_2\text{M}(\text{THF})_2)]$. The heterolepetic compounds $[\{(i\text{Pr})_2\text{ATI}\}\text{M}\{\text{N}(\text{SiMe}_3)_2\}(\text{THF})_2)]$ were used as catalysts for the intramolecular hydroamination/cyclization reaction of nonactivated aminoalkenes. A decrease in the rate with increasing ion radius of the center metal is observed for the alkaline earth elements. The ytterbium complex, which is oxidized during the catalytic conversion, is also an efficient precatalyst for the hydroamination/cyclization reaction.

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. At the present time most amines are made in multistep syntheses, and as such 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) offers an attractive alternative to give nitrogen-containing molecules.[1,2] It has been shown that the hydroamination reaction can be catalyzed by d-[3–5] and f-block[2k,6–14] transition metals, alkali metals,[15]and more recently by copper,[16] silver,[17] gold,[18] and zinc.[19] 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 an advantage of greater polar functional group compatibility. However, most of these catalysts are based on the relatively expensive platinum metals[4] or on nickel,[4] 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. Therefore, there is a demand for new catalysts for the hydroamination. In this context M. S. Hill et al.[20] lately reported the *β*-diketiminato calcium bis(trimethylsilyl)amide $[\{\text{HC}(\text{C}(\text{Me})_2\text{N-}2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)_2\}\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}(\text{THF})]$ as an efficient catalytic

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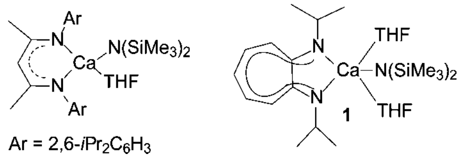
10.1021/om701014d CCC: $40.75

Scheme 1



system (Scheme 1). Inspired by this work we recently reported on the calcium amido complexes [(*i*PrAT)Ca{N(SiMe$_3$)$_2$}(THF)]$_2$ (*i*PrAT = 2-(isopropylamino)troponate) and [{(*i*Pr)$_2$ATI}Ca{N(SiMe$_3$)$_2$}(THF)$_2$] (**1**) ((*i*Pr)$_2$ATI = *N*-isopropyl-2-(isopropylamino)troponiminate) (Scheme 1), which showed for some substrates a similar activity to the β-diketiminato system as catalysts for hydroamination.[21] Now, we are interested in extending this work and introducing the aminotroponiminate ligand into the chemistry of the heavier alkaline earth elements strontium and barium. Moreover, it is well established that the reactivity and coordination behavior of the divalent lanthanide metals and the heavier alkaline earth metals is somewhat similar.[22] This similarity in coordination chemistry originates from the similar ion radii (for CN 6 (pm): Ca^{2+} 100, Yb^{2+} 102, Sr^{2+} 118, Eu^{2+} 117, Ba^{2+} 135).[23] Therefore, we also wanted to synthesize aminotroponiminate complexes of divalent europium and ytterbium.

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. Ether solvents (tetrahydrofuran and ethyl ether) were 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 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 JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane and 85% phosphoric acid (^{31}P NMR), respectively. Raman spectra were performed on a Bruker RFS 100. Elemental analyses were carried out with an Elementar Vario EL III. SrI$_2$ and BaI$_2$ were purchased from Aldrich Inc. EuI$_2$(THF)$_2$,[24] YbI$_2$(THF)$_2$,[25] and [{(*i*Pr)$_2$ATI}K][26] were prepared according to literature procedures.

General Procedure for the Synthesis of [{(*i*Pr)$_2$ATI}M{N(SiMe$_3$)$_2$}(THF)$_2$)] (M = Sr (2), Eu (5), Yb (6)). THF was condensed at −196 °C onto a mixture of 0.5 mmol of MI$_2$(THF)$_2$ (M = Yb, Eu) or SrI$_2$, 121 mg (0.5 mmol) of [K{(*i*Pr)$_2$ATI}], and 100 mg (0.5 mmol) of KN(SiMe$_3$)$_2$. The mixture was then stirred for 36 h at room temperature. The red-colored solution was filtered to remove potassium iodide, and then the solvent was removed *in vacuo*. Finally, the remaining powder was washed with pentane.

2: crystallized from hot THF/toluene (1:1) mixture. Yield: 100 mg (34%), red-colored crystals. ^{1}H NMR (d_8-THF, 400 MHz, 25 °C): δ 0.07 (s, 18H, N(SiMe$_3$)$_2$), 1.44 (d, 12H, CH$_3$, J(H,H) = 6.3 Hz), 1.90 (m, 8H, THF, J(H,H) = 6.5 Hz), 3.75 (m, 8H, THF, J(H,H) = 6.5 Hz), 3.94 (sept, 2H, (CH$_3$)$_2$C*H*, J(H,H) = 6.3 Hz), 5.78 (t, 1H, H$_{\text{ring}}$, J(H,H) = 8.8 Hz), 6.12 (d, 2H, H$_{\text{ring}}$, J(H,H) = 11.4 Hz), 6.64–6.72 (dd, 2H, H$_{\text{ring}}$, J(H,H) = 8.8 Hz, 11.4 Hz). ^{13}C{^{1}H} NMR (d_8-THF, 100.4 MHz, 25 °C): δ 5.8 (N(Si(*C*H$_3$)$_2$)), 24.1 (*C*H$_3$), 26.3 (THF), 49.8 ((CH$_3$)$_2$*C*H), 68.2 (THF), 108.6 (*C*$_{\text{ring}}$), 110.9 (*C*$_{\text{ring}}$), 133.4 (*C*$_{\text{ring}}$), 163.8 (*C*$_{\text{ring}}$). ^{29}Si NMR (C$_6$D$_6$, 79.30 MHz, 25 °C): δ −65.12. Anal. Calcd for C$_{27}$H$_{53}$SrSi$_2$N$_3$O$_2$ (595.52): C 54.46, H 8.97, N 7.06. Found: C 54.32, H 9.02, N 6.81.

5: crystallized from THF/pentane (1:3). Yield: 50 mg (17%), red-colored crystals. MS (EI, 8 kV, 230 °C): *m*/*z* (%) 661 [C$_{27}$H$_{53}$EuSi$_2$N$_3$O$_2$ + 2H]$^+$ (30), 516 [C$_{27}$H$_{53}$EuSi$_2$N$_3$O$_2$ − 2 THF + H]$^+$ (1), 354 [[(*i*Pr)$_2$ATI]Eu − H]$^+$ (11), 204 [(*i*Pr)$_2$ATI + H]$^+$ (45), 189 [(*i*Pr)$_2$ATI − Me + H]$^+$ (41), 161 [(*i*Pr)$_2$ATI − *i*Pr + H]$^+$ (64), 146 [(*i*Pr)$_2$ATI − *i*Pr − Me + H]$^+$ (100). Anal. Calcd for C$_{27}$H$_{53}$EuSi$_2$N$_3$O$_2$·THF (587.76): C 47.00, H 7.72, N 7.15. Found: C 46.41, H 7.63, N 6.56.

6: crystallized from THF/pentane (1:3). Yield: 110 mg (36%), tiny brown-colored crystals. ^{1}H NMR (C$_6$D$_6$, 400 MHz, 25 °C): δ 0.37 (s, 18H, N(SiMe$_3$)$_2$), 1.23 (br, 8H, THF), 1.33 (br, 12H, CH$_3$), 3.39 (br, 8H, THF), 3.86 (br, 2H, (CH$_3$)$_2$C*H*), 6.18 (br, 1H, H$_{\text{ring}}$), 6.31 (br, 2H, H$_{\text{ring}}$), 6.99 (br, 2H, H$_{\text{ring}}$). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.4

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Table 1. Crystallographic Details of [{(*i*Pr)$_2$ATI}Sr{N(SiMe$_3$)$_2$}(THF)$_2$)] (2), [{(*i*Pr)$_2$ATI}$_2$Sr(THF)$_2$)] (3), [{(*i*Pr)$_2$ATI}$_2$Ba(THF)$_2$)] (4), [{(*i*Pr)$_2$ATI}Eu{N(SiMe$_3$)$_2$}(THF)$_2$)] (5), and [{(*i*Pr)$_2$ATI}Yb{N(SiMe$_3$)$_2$}(THF)$_2$)] (6)[a]

	2	3	4	5	6
formula	$C_{27}H_{53}N_3O_2Si_2Sr$	$C_{34}H_{54}N_4O_2Sr$	$C_{34}H_{54}BaN_4O_2$	$C_{27}H_{53}EuN_3O_2Si_2$	$C_{27}H_{53}N_3O_2Si_2Yb$
fw	595.52	638.43	688.15	659.86	680.94
space group	$P2_1$ (No. 4)	*Pbcn* (No. 60)	*Pbcn* (No. 60)	$P2_1$ (No. 4)	$P2_1$ (No. 4)
a, Å	10.0783(8)	15.9678(15)	15.5788(10)	10.0714(8)	9.9810(5)
b, Å	14.8443(10)	11.0432(8)	11.1267(7)	14.8719(9)	14.7544(11)
c, Å	11.2553(10)	19.2699(15)	19.8676(11)	11.2287(9)	11.2266(7)
β, deg	95.166(7)			95.272(6)	96.299(5)
V, Å^3	1677.0(2)	3398.0(5)	3443.9(4)	1674.7(2)	1643.3(2)
Z	2	4	4	2	2
density, g/cm^3	1.179	1.248	1.327	1.309	1.376
radiation	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
μ, mm^{-1}	1.704	1.621	1.187	1.969	2.944
absorp corr	numerical	numerical	numerical	numerical	numerical
no. of reflns collected	8688	8644	13 055	9306	8725
no. of unique reflns	5619 [R_{int} = 0.0400]	3003 [R_{int} = 0.0874]	3027 [R_{int} = 0.0381]	5700 [R_{int} = 0.0295]	5752 [R_{int} = 0.0730]
no. of obsd reflns	5046	1996	2327	5308	5304
no. of data; params	5619; 325	3003; 190	3027; 190	5700; 325	5752; 326
GOOF on F^2	1.003	1.002	1.001	1.003	1.034
absolute struct param (Flack)	−0.005(6)			−0.007(9)	−0.01(2)
R_1[b]; wR_2[c]	0.0377; 0.0872	0.0466; 0.1013	0.0252; 0.0678	0.0207; 0.0536	0.0555; 0.1680

[a] All data collected at 200 K. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

MHz, 25 °C): δ 5.7 (N(Si(*C*H$_3$)$_2$)), 22.7 (*C*H$_3$), 25.4 (THF), 48.1 ((CH$_3$)$_2$*C*H), 68.7 (THF), 111.2 (C_{ring}), 113.8 (C_{ring}), 133.6 (C_{ring}), 162.9 (C_{ring}). ^{29}Si NMR (C_6D_6, 79.30 MHz, 25 °C): δ −64.63. Anal. Calcd for $C_{27}H_{53}YbSi_2N_3O_2 \cdot$(THF) (608.84): C 45.37, H 7.45, N 6.90. Found: C 44.39, H 7.35, N 5.79.

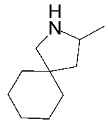
4.3.3. General Procedure for the Synthesis of [{(*i*Pr)$_2$ATI}$_2$M(THF)$_2$] (M = Sr (3), Ba (4)). THF was condensed at −196 °C onto a mixture of 0.5 mmol of MI$_2$ (M = Sr, Ba) and 242 mg (1.0 mmol) of [K{(*i*Pr)$_2$ATI}]. The mixture was then stirred for 36 h at room temperature. The red-colored solution was filtered to remove potassium iodide, and then the solvent was removed *in vacuo*. Finally, the remaining powder was washed with pentane.

3: crystallized from THF/pentane (1:3). Yield: 120 mg (38%), yellow-colored crystals. ^{1}H NMR (d_8-THF, 400 MHz, 25 °C): δ 1.16 (d, 24H, CH$_3$, J(H,H) = 6.5 Hz), 1.72 (m, 8H, THF), 3.57 (m, 8H, THF), 3.74 (sept, 4H, (CH$_3$)$_2$C*H*, J(H,H) = 6.5 Hz), 5.53 (t, 2H, H_{ring}, J(H,H) = 8.8 Hz), 5.85 (d, 4H, H_{ring}, J(H,H) = 11.5 Hz), 6.48 (dd, 4H, H_{ring}, J(H,H) = 8.8 Hz, 11.5 Hz). ^{13}C{^{1}H} NMR (d_8-THF, 100.4 MHz, 25 °C): δ 23.9 (*C*H$_3$), 26.4 (THF), 50.5 ((CH$_3$)$_2$*C*H), 68.2 (THF), 108.2 (C_{ring}), 109.6 (C_{ring}), 133.0 (C_{ring}), 163.7 (C_{ring}). MS (EI, 8KV, 130 °C): m/z (%) 494 [M − 2 THF]$^+$ (2.50), 291 [M − (*i*Pr)$_2$ATI − 2 THF]$^+$ (3), 204 [(*i*Pr)$_2$ATI + H]$^+$ (98), 189 [(*i*Pr)$_2$ATI − Me + H]$^+$ (100), 161 [(*i*Pr)$_2$ATI − *i*Pr + H]$^+$ (77), 72 [C_4H_8O]$^+$ (94). Anal. Calcd for $C_{34}H_{54}N_4O_2Sr$ (638.44): C 63.96, H 8.53, N 8.78. Found: C 63.48, H 8.41, N 8.81.

4: crystallized from hot THF. Yield: 90 mg (26%), yellow-colored crystals. ^{1}H NMR (d_8-THF, 400 MHz, 25 °C): δ 1.21 (d, 24H, CH$_3$, J(H,H) = 6.4 Hz), 1.73 (m, 8H, THF), 3.56 (m, 8H, THF), 3.82 (sept, 4H, (CH$_3$)$_2$C*H*, J(H,H) = 6.4 Hz), 5.48 (t, 2H, H_{ring}, J(H,H) = 8.7 Hz), 5.81 (d, 4H, H_{ring}, J(H,H) = 11.5 Hz), 6.45 (dd, 4H, H_{ring}, J(H,H) = 8.7 Hz, 11.5 Hz). ^{13}C{^{1}H} NMR (d_8-THF, 100.4 MHz, 25 °C): δ 24.1 (*C*H$_3$), 26.4 (THF), 50.2 ((CH$_3$)$_2$*C*H), 68.2 (THF), 107.7 (C_{ring}), 109.5 (C_{ring}), 132.9 (C_{ring}), 164.1 (C_{ring}). MS (EI, 8KV, 200 °C): m/z (%) 544 [M − 2 THF + H]$^+$ (9), 341 [M − (*i*Pr)$_2$ATI − 2 THF + H]$^+$ (44), 204 [(*i*Pr)$_2$ATI + H]$^+$ (81), 189 [(*i*Pr)$_2$ATI − Me + H]$^+$ (100), 161 [(*i*Pr)$_2$ATI − *i*Pr + H]$^+$ (78).

General Procedure for the Hydroamination Reaction (NMR scale reaction). The catalyst was weighed under argon gas into an NMR tube. C_6D_6 (~0.7 mL) was condensed into the NMR tube, and the mixture was frozen to −196 °C. The reactant was injected onto the solid mixture, and the whole sample was melted and mixed just before the insertion into the core of the NMR machine (t_0). The ratio between the reactant and the product was exactly calculated by comparison of the integrations of the corresponding signals. The N(Si*Me$_3$*)$_2$ groups and for some selected samples ferrocene were used as an internal standard for the kinetic measurements.

For the intramolecular hydroamination/cyclization reactions, the substrates 2,2-diphenylpent-4-en-1-amine,[27] (1-allylcyclohexyl)-methanamine,[27] 2,2-dimethylpent-4-en-1-amine,[28] hex-5-en-2-amine,[28] 4-penten-1-amine,[28] 2,2-dimethylhex-5-en-1-amine,[28] and (*E*)-5-phenyl-2,2-dimethyl-1-amino-4-pentene[29] were synthesized according to literature procedure. Spectra of the products shown in Table 3 are consistent with literature data.[27–29]



Preparative Scale Hydroamination/Cyclization Reaction. A 300 mg portion of 2-cyclohexyl-1-amino-pent-4-ene was added to 15 mg (0.025 mmol) of **2** in C_6D_6. The reaction mixture was stirred overnight. The reaction mixture was quenched by the addition of water, and the product was extracted with ether. The organic layer was washed with water and dried over MgSO$_4$. The solvent was evaporated and distilled to give pure product in 90% yield. The ^{1}H NMR spectrum of the product was consistent with literature data.[29]

X-ray Crystallographic Studies of 2–6. Crystals of **2** were grown from THF/toluene (1:1); crystals of **3**, **5**, and **6** were obtained from THF/*n*-pentane (1:3); crystals of **4** were grown from hot THF. A suitable crystal was covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the −73 °C cold N$_2$ stream of a Stoe IPDS 2T diffractometer. Subsequent computations were carried out on an Intel Core 2 Duo PC.

All structures were solved by the Patterson method (SHELXS-97).[30] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements

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(27) Ryu, J.-S.; Li, G. Y.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 12584–12605.

(28) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275–294.

(29) Gribkov, D. V.; Hultzsch, K. C.; Hampel, F. *J. Am. Chem. Soc.* **2006**, *128*, 3748–3759.

(30) Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*; University of Göttingen: Germany, 1997.

Table 2. Selected Bond Lengths and Angles of [{(*i*Pr)$_2$ATI}Sr{N(SiMe$_3$)$_2$}(THF)$_2$)] (2), [{(*i*Pr)$_2$ATI}$_2$Sr(THF)$_2$)] (3), [{(*i*Pr)$_2$ATI}$_2$Ba(THF)$_2$)] (4), [{(*i*Pr)$_2$ATI}Eu{N(SiMe$_3$)$_2$}(THF)$_2$)] (5), and [{(*i*Pr)$_2$ATI}Yb{N(SiMe$_3$)$_2$}(THF)$_2$)] (6)

2		3		4		5		6	
Bond Lengths (Å)									
Sr−N1	2.554(3)	Sr−N1	2.669(3)	Ba−N1	2.801(2)	Eu−N1	2.540(3)	Yb−N1	2.442(10)
Sr−N2	2.568(3)	Sr−N2	2.593(3)	Ba−N2	2.744(2)	Eu−N2	2.558(3)	Yb−N2	2.438(10)
Sr−N3	2.482(3)	Sr−O	2.654(3)	Ba−O	2.812(2)	Eu−N3	2.468(3)	Yb−N3	2.380(12)
Sr−O1	2.569(3)					Eu−O1	2.573(3)	Yb−O1	2.459(11)
Sr−O2	2.573(3)					Eu−O2	2.600(3)	Yb−O2	2.498(9)
Bond Angles (deg)									
N1−Sr−N2	63.55(10)	N1−Sr−N2	61.14(9)	N1−Ba−N2	57.40(5)	N1−Eu−N2	63.45(10)	N1−Yb−N2	67.6(4)
N1−Sr−N3	105.75(11)	N1−Sr−N1′	164.45(12)	N1−Ba−N1′	162.00(8)	N1−Eu−N3	105.36(10)	N1−Yb−N3	103.1(4)
N2−Sr−N3	129.20(11)	N1−Sr−N2′	107.62(9)	N1−Ba−N2′	109.43(6)	N2−Eu−N3	127.86(12)	N2−Yb−N3	125.7(4)
N1−Sr−O1	86.45(11)	N2−Sr−N2′	96.64(12)	N2−Ba−N2′	97.58(9)	N1−Eu−O1	86.68(10)	N1−Yb−O1	86.2(4)
N1−Sr−O2	161.17(10)	N1−Sr−O	81.66(9)	N1−Ba−O	82.05(6)	N1−Eu−O2	160.65(10)	N1−Yb−O2	162.8(3)
N2−Sr−O1	93.22(11)	N1−Sr−O′	109.65(9)	N1−Ba−O′	110.73(7)	N2−Eu−O1	94.59(12)	N2−Yb−O1	96.6(4)
N2−Sr−O2	104.33(10)	N2−Sr−O	87.28(8)	N2−Ba−O	85.95(7)	N2−Eu−O2	104.25(10)	N2−Yb−O2	103.1(4)
N3−Sr−O1	137.16(11)	N2−Sr−O′	170.71(9)	N2−Ba−O′	168.12(6)	N3−Eu−O1	137.08(11)	N3−Yb−O1	137.2(4)
N3−Sr−O2	93.09(10)	O−Sr−O′	90.12(13)	O−Ba−O′	92.90(10)	N3−Eu−O2	93.99(10)	N3−Yb−O2	94.0(4)

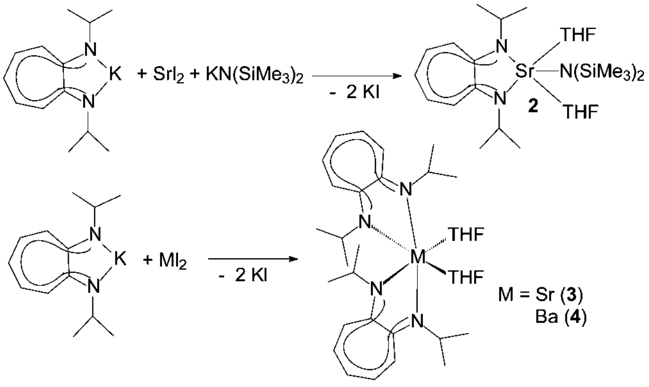
were carried out by using full-matrix least-squares techniques on F, minimizing the function $(F_o - F_c)^2$, where the weight is defined as $4F_o^2/2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes using the program SHELXL-97.[31] In the final cycles of each refinement, all non-hydrogen atoms except the disordered atoms C25A and C25B in **2** and C26A and C26B in **5** were assigned anisotropic temperature factors. The hydrogen atom contributions were calculated, but not refined. The final values of refinement parameters are given in Table 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, 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 no. CCDC-656438–656442. 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

Alkaline Earth Metal Compounds. Reaction of anhydrous strontium diiodide with the potassium salts KN(SiMe$_3$)$_2$ and [{(*i*Pr)$_2$ATI}K] ((*i*Pr)$_2$ATI = *N*-isopropyl-2-(isopropylamino)troponiminate) in a 1:1:1 molar ratio followed by crystallization from a THF/toluene mixture led selectively to a product of composition [{(*i*Pr)$_2$ATI}Sr{N(SiMe$_3$)$_2$}(THF)$_2$] (**2**) (Scheme 2). Compound **2** can be considered as the heavier analogue of the calcium complex [{(*i*Pr)$_2$ATI}Ca{N(SiMe$_3$)$_2$}(THF)$_2$] (**1**).[21] The diaminotroponiminate complex [{(*i*Pr)$_2$ATI}$_2$Sr(THF)$_2$] (**3**) was obtained by reacting SrI$_2$ with 2 equiv of [{(*i*Pr)$_2$ATI}K] in THF followed by crystallization from THF/*n*-pentane (1:3) (Scheme 2). The new complexes have been characterized by standard analytical/spectroscopic techniques, and the solid-state structures of both compounds were established by single-crystal X-ray diffraction.

The ^{1}H and ^{13}C NMR spectra of compounds **2** and **3** point to a symmetrical coordination of the {(*i*Pr)$_2$ATI}$^-$ anion in solution. The signals of the isopropyl C*H* group of **2** (δ 3.94 ppm) and **3** (δ 3.73 ppm) are well-resolved into a septet and show a downfield shift compared to that of the starting material [{(*i*Pr)$_2$ATI}K] (δ 3.67 ppm).[26] Moreover a large singlet is observed (δ 0.07 ppm) for the N(SiMe$_3$)$_2$$^-$ group of **2**.

Scheme 2



Compound **2** crystallizes in the chiral monoclinic space group $P2_1$ having two molecules of **2** in the unit cell (Figure 1). Data collection parameters and selected bond lengths and angles are given in Tables 1 and 2, respectively. The strontium atom is 5-fold coordinated by the bidentate chelating {(*i*Pr)$_2$ATI}$^-$ ligand, the {N(SiMe$_3$)$_2$}$^-$ group, and two molecules of THF. The resulting coordination polyhedron can be considered as distorted trigonal bipyramidal, having the atoms N1 and O2 in the axis. The N1−Sr−O2 angle is 161.17(10)°. The distortion of the coordination polyhedron is a result of the small bite angle of the chelating {(*i*Pr)$_2$ATI}$^-$ ligand (N1−Sr−N2 63.55(10)°). The {(*i*Pr)$_2$ATI}$^-$ ligand is symmetrically attached to the metal center resulting in Sr−N bond lengths of Sr−N1 2.554(3) Å

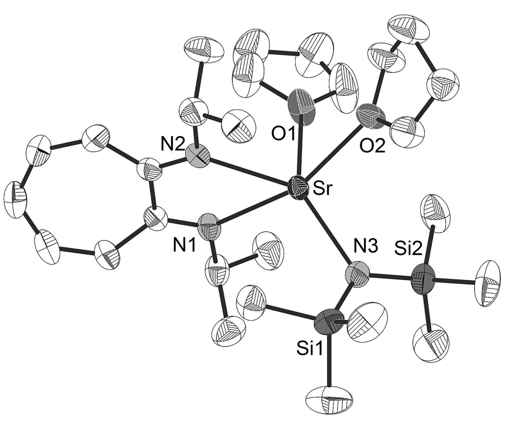


Figure 1. Perspective ORTEP view of the molecular structure of **2**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity.

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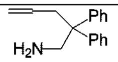
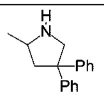
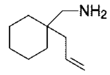
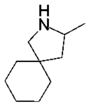
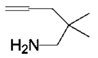
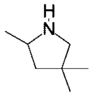
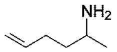
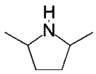
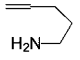
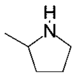
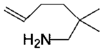
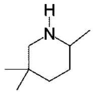
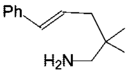
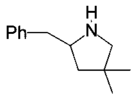
[31] Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Germany, 1997.

Table 3. Hydroamination/Cyclization Reaction of Terminal Aminoalkenes Catalyzed by 1, 2, and 6[a]

Entry	Substrate	Product	Cat	mol% Cat	t h	Yield %^{b}
1			**1**^{d}	10	0.25	99^{c}
				2	1	99^{c}
			2	3	1.5	99
			6	3	0.25	99^{c}
2			**1**^{d}	2	0.6	99^{c}
						93^{e}
			2	3	9	80
						90^{e}
			6	3	1	99^{c}
3			**1**^{d}	2	3.5	>95^{c}
			2	3	72	90
			6	2	5.5	40^{c}
					22	50^{c}
					48	70^{c}
					72	>80^{c}
4			**1**^{d}	2	24	>90^{g}
			2	8	28	>80^{h}
			6	5	21	30^{c}
					72	50^{c}
					120	70^{c}
5			**1**^{d}	10	40	>90^{c}
			2	10	72	70
					10	>90^{f}
			6	5	170	-
6			**1**^{d}	8	47	20^{c}
					15	>90$^{c, f}$
			2	15	15	>80^{f}
7			**1**	10	0.16	80^{c}
			2	10	0.16	80^{c}

[a] Reaction at room temperature in 0.6–0.7 mL of C_6D_6. [b] Calculated by ^{1}H NMR. [c] Ferrocene as additional internal standard. [d] Data taken from ref 21. [e] Isolated yield. [f] Reaction at 60 °C. [g] *cis*:*trans* ratio 1:4. [h] *cis*:*trans* ratio 7:3.

and Sr−N2 2.568(3) Å. Since **2** is a chiral molecule, which crystallizes in a chiral space group, the single crystals of **2** contain enantiomerically pure complexes. The chirality in **2** is caused by the arrangement of the ligands around the metal center. Since there is no diastereotopic splitting of the isopropyl signals seen in the NMR spectra, the observed chirality seems to be a solid-state effect only.

Compound **3** crystallizes in the orthorhombic space group *Pbca*, having four molecules of **3** in the unit cell (Figure 2). Data collection parameters and selected bond lengths and angles are given in Tables 1 and 2, respectively. In contrast to compound **2** in compound **3** the strontium atom is hexacoordinated by two $\{(i\text{Pr})_2\text{ATI}\}^-$ ligands and two molecules of THF. Thus, the coordination polyhedron is best described as a distorted octahedron. A crystallographic *C*2 axis passes through the strontium atom that bisects the octahedron. The tight chelating N1−Sr−N2 angle of 61.14(9)°, which is in the range of the one observed in compound **2**, causes the distortion of the octahedron. This also influences the angles of the *trans*-located atoms (N1−Sr−N1′ 164.45(12)° and N2−Sr−O′ 170.71(9)°). Only the angle between the THF molecules is close to 90° (O−Sr−O′ 90.12(13)°). The Sr−N and Sr−O bond distances are in the expected range.[32]

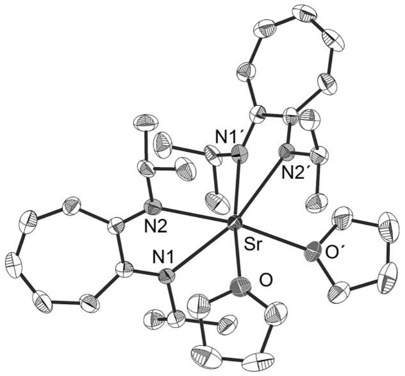


Figure 2. Perspective ORTEP view of the molecular structure of **3**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity.

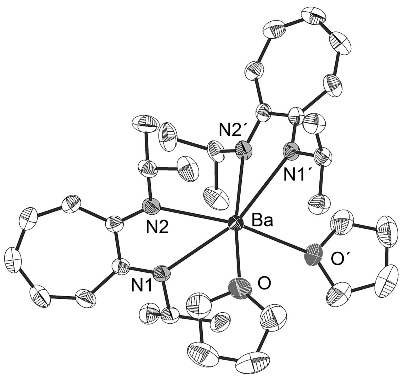


Figure 3. Perspective ORTEP view of the molecular structure of **4**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity.

A similar approach as used for the synthesis of **2** but starting from anhydrous barium diiodide does not result in the expected compound $[\{(i\text{Pr})_2\text{ATI}\}\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}(\text{THF})_2)]$. Instead the diaminotroponiminate complex $[\{(i\text{Pr})_2\text{ATI}\}_2\text{Ba}(\text{THF})_2)]$ (**4**), which is the analogue to compound **3**, was isolated. Also the reaction of $[\text{Ba}\{\text{N}(\text{SiMe}_3)_2\}_2]$ and $\{(i\text{Pr})_2\text{ATI}\}\text{H}$ does not result in the desired compound but in complex **4**. Compound **4** was then synthesized in a rational approach by reacting BaI_2 with 2 equiv of $[\{(i\text{Pr})_2\text{ATI}\}\text{K}]$ in THF (Scheme 2). The ^{1}H and ^{13}C NMR spectra of compounds **4** point to a symmetrical coordination of the $\{(i\text{Pr})_2\text{ATI}\}^-$ anion in solution. The signal of the isopropyl C*H* group (δ 3.82 ppm) is well-resolved into a septet. The structure of compound **4** was also established in the solid state by single-crystal X-ray diffraction (Figure 3). As result of the larger ion radius of Ba^{2+} compared to Sr^{2+}, usually the coordination number of the barium atom is higher.[33] In contrast to these observations compounds **3** and **4** are isostructural to each other (Table 1), and thus the barium atom is also 6-fold

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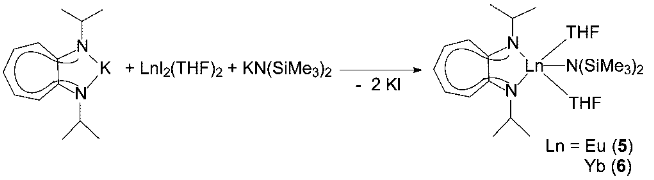
(32) Roesky, P. W. *Inorg. Chem.* **2006**, *45*, 798–802.

(33) Hanusa, T. P.; Willams, I. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J. , Eds.; Parkin G. F., Volume Ed.; Elsevier, Amsterdam, 2003; Vol. 3, pp 1–92..

Scheme 3



coordinated by two $\{(i\mathrm{Pr})_2\mathrm{ATI}\}^-$ ligands and two molecules of THF. The Ba−N (Ba−N1 2.801(2) Å, Ba−N2 2.744(2) Å) and Ba−O bond (Ba−O 2.812(2) Å) distances are in the expected range.[34]

Divalent Lanthanide Compounds. As already mentioned in the Introduction, as a result of the similar ion radii, it is well established that the reactivity and coordination behavior of the divalent lanthanide metals and the heavier alkaline earth metals is somewhat similar. Therefore, we expected a certain relationship between **1** and an analogous ytterbium(II) compound and between **2** and a related europium(II) compound, whereas barium(II) may be too large to be part of this analogy. To prove our expectations, $\mathrm{LnI_2(THF)_2}$ (Ln = Eu, Yb) were reacted with $\mathrm{KN(SiMe_3)_2}$ and $[\{(i\mathrm{Pr})_2\mathrm{ATI}\}\mathrm{K}]$ in a 1:1:1 molar ratio. After crystallization the desired amido complexes of composition $[\{(i\mathrm{Pr})_2\mathrm{ATI}\}\mathrm{Ln}\{\mathrm{N(SiMe_3)_2}\}(\mathrm{THF})_2)]$ (Ln = Eu (**5**), Yb (**6**)) were obtained (Scheme 3). Compounds **5** and **6** crystallize in the chiral monoclinic space group $P2_1$ with two molecules in the unit cell (Figure 4, shown is compound **6** only). Data collection parameters and selected bond lengths and angles are given in Tables 1 and 2, respectively. Interestingly, not only are compounds **5** and **6** isostructural to each other but they are also isostructural to compounds **1** and **2**. As already observed for compound **3** and **4**, the expected raise of the coordination number with increasing ionic radius is not seen. Nevertheless, the bonding distances within the distorted trigonal bipyramidal coordination polyhedron formed by the bidentate chelating $\{(i\mathrm{Pr})_2\mathrm{ATI}\}^-$ ligand, the $\{\mathrm{N(SiMe_3)_2}\}^-$ group, and two molecules of THF are in the expected range.

The multinuclear NMR data of the diamagnetic compound **6** are consistent with the solid-state structure. The ^{1}H NMR spectrum of compound **6** shows a characteristic sharp singlet for the $\mathrm{N(SiMe_3)_2}^-$ group at δ 0.37 ppm. The ^{1}H spectrum also points to a symmetrical coordination of the $\{(i\mathrm{Pr})_2\mathrm{ATI}\}^-$ anion in solution. The signal of the isopropyl C*H* group is observed at δ 3.86 ppm.

Hydroamination/Cyclization Catalysis. In our previous contribution we reported about the catalytic activity of the Ca compound **1** in the intramolecular hydroamination/cyclization reaction.[21] Now, our intention is to evaluate the catalytic activity of the heterolepetic compounds **2** and **6** in comparison to complex **1** for two reasons (Table 3). In the lanthanide-catalyzed hydroamination of aminoolefins usually the rates increase with increasing ion radius of the center metal.[6,35] Therefore, we were interested in a comparison of compounds **1** and **2**. Moreover, S. Harder et al. pointed out that even structurally very similar calcium and ytterbium compounds may show a significantly different activity in catalysis.[22d] This inspired us also to compare the activity of compounds **1** and **6**. By using the europium compound **5** as catalyst, the NMR signals were, as a result of the strong paramagnetism, too broad to record reliable kinetics. In our substrate screening we focused on the challenging nonactivated aminoalkenes. The rigorously anaerobic reaction of the catalyst with dry, degassed aminoalkenes proceeds regiospecifically. It turned out that all substrates are converted to the cyclic product at mild reaction conditions. Using compound **2** as catalyst all substrates leading to five-membered rings (entries 1–5 and 7) could be cyclized in high yields at room temperature. Substrates bearing bulky geminal substituents in the β-position to the amino group (Thorpe−Ingold effect)[36] could be cyclized with low catalyst loadings of 3 mol % within short reaction times (entries 1 and 2). Clearly compound **2** is significantly less active then **1**. Thus, in contrast to the observation in lanthanide chemistry the smaller the element formed, calcium in our case, the more active the catalyst. The transformations were also efficient for an internal olefin in the case of the “activated” styrene conversion (entry 7). In contrast, the more challenging substrates (entries 4–6) could only be cyclized by using higher catalyst loadings of compound **2**. The yields for the catalytic reactions were determined by ^{1}H NMR spectroscopy for compound **2**. It could be shown that $\mathrm{HN(SiMe_3)_2}$ was formed in stoichiometric ratios. We anticipate that the $\mathrm{N(SiMe_3)_2}^-$ group of the catalysts is protonated by the substrate in the initial step, forming a catalytically active species in which the substrate is bound as an amido group onto the metal atom.

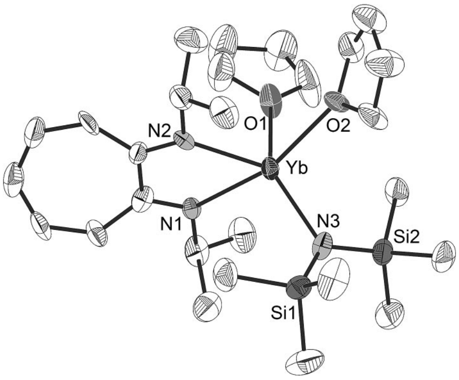


Figure 4. Perspective ORTEP view of the molecular structure of **6**. Thermal ellipsoids are drawn to encompass 50% probability. Hydrogen atoms are omitted for clarity.

The differences in rate for compound **6** with respect to compound **2** are of course substrate dependent. The ytterbium compound **6** shows a comparable activity to compound **2** for substrates having a bulky substituent at the β-position (entries 1 and 2). For more challenging substrates (entry 3 and 4), significantly low activity at room temperature is observed for **6** in comparison to **2**. For the substrate 1-aminopent-4-ene (entry 5) no reaction was observed even at higher temperature and the color change was observed from grayish to red color. The yields for compound **6** were determined using ferrocene as an internal standard. The accurate determination of the rates for compound **6** is limited by the resulting paramagnetically active ytterbium species, which cause some line broadening of the ^{1}H NMR signals. Obviously part or all of the precatalyst **6** is oxidized *in situ* during the catalytic conversion. The resulting trivalent ytterbium complex is an efficient precatalyst, but as a result of the different oxidation state a comparison with the divalent alkaline earth metal complexes is restricted to the rates.

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Summary

In summary, mono- and diaminotroponiminate complexes of the heavier alkaline earth elements and the related divalent lanthanides of composition [{(*i*Pr)$_2$ATI}M{N(SiMe$_3$)$_2$}(THF)$_2$)] (M = Sr, Eu, Yb) and [{(*i*Pr)$_2$ATI}$_2$M(THF)$_2$)] (M = Sr, Ba) were prepared. The NMR spectra of all compounds point to a symmetrical coordination of the {(*i*Pr)$_2$ATI}$^-$ anion in solution. All new compounds were characterized by single-crystal X-ray diffraction. Independent of the ionic radius of the center metal, all monoaminotroponiminate complexes [{(*i*Pr)$_2$ATI}M{N(SiMe$_3$)$_2$}(THF)$_2$)] including the previously reported Ca analogue are isostructural. The same phenomenon is observed for [{(*i*Pr)$_2$ATI}$_2$M(THF)$_2$)]. The heterolepetic compounds [{(*i*Pr)$_2$ATI}M{N(SiMe$_3$)$_2$}(THF)$_2$)] were evaluated in comparison to complex [{(*i*Pr)$_2$ATI}Ca{N(SiMe$_3$)$_2$}(THF)$_2$)] in the intramolecular hydroamination/cyclization reaction of nonactivated aminoalkenes. It could be shown that the strontium complex is significantly slower than the analogous calcium compound. A decrease of the rate with increasing ion radius of the center metal is in contrast to the observations in lanthanide chemistry. The ytterbium complex is (partly) oxidized during the catalytic conversion, and the difference in the rate with respect to the calcium compound is substrate dependent.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **2–6** are available free of charge via the Internet at http://pubs.acs.org.

OM701014D