Angewandte Chemie International Edition

DOI: 10.1002/anie.201200364

Synthetic Methods

When Bigger Is Better: Intermolecular Hydrofunctionalizations of Activated Alkenes Catalyzed by Heteroleptic Alkaline Earth Complexes**

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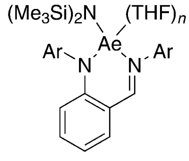
Dedicated to Dr. Christian Bruneau and Dr. Hubert Le Bozec on the occasion of their 60th birthdays

Catalyzed hydrofunctionalizations of unsaturated substrates are of tremendous interest, primarily because of their atom efficiency.[1] Intramolecular catalytic cyclohydroamination of aminoalkenes can be efficiently promoted by d^0 complexes of the heavy alkaline-earth (Ae) metals,[2,3] typically Ca and in rare cases Sr, as recently exemplified by the groups of Hill,[4] Ward,[5] and Roesky.[6] The catalytic activity of these complexes, which are based on large, electropositive elements (ionic radii: Ca^{2+}(6), 1.00 Å; Sr^{2+}(6), 1.18 Å),[7] compares well with that of isoelectronic trivalent rare-earth catalysts.[8] Through their seminal studies, Hill and co-workers have shown that the stable β-diketiminate compound $[\{L^3\}CaN(SiMe_3)_2(THF)]$[9–11] ($\{L^3\}H = H_2C\{C(Me)N\text{-}2,6\text{-}(i\Pr)_2C_6H_3\}_2$; THF = tetrahydrofuran) is highly versatile and effective not only for intramolecular hydroamination,[4] but also for other reactions[2,12] such as the intermolecular hydrophosphination of alkynes and activated alkenes,[12a] a transformation which has not been catalyzed by trivalent rare-earth complexes thus far.[8a,13]

Few examples of intermolecular hydroamination reactions catalyzed by Ae complexes are known, and they involve activated alkenes, that is, vinyl arenes and conjugated dienes. Very recently, Emge and Hultzsch reported a heteroleptic chiral magnesium phenolate complex which displayed an outstanding performance in the enantioselective intra- and intermolecular hydroamination of terminal aminoalkenes and styrene derivatives, respectively.[3d] Prior to this, Hill and co-workers had employed the homoleptic precursors $[\{M[N(SiMe_3)_2]_2\}_2]$ (M = Ca, Sr) to illustrate theoretical calculations on related, yet heteroleptic, systems.[14] In the original study, the authors showed that the activity of Ae catalysts (M = Mg, Ca, Sr, Ba) does not increase linearly with the size of the metal (Mg^{2+}(6), 0.72 Å; Ba^{2+}(6), 1.35 Å). Calculations showed that a model Sr heteroleptic complex should be more active in the amination of ethylene with ammonia than its Ca derivative (which in turn should be far more active than the Mg analogue), but they also suggested that the trend should not be respected with Ba. Experimental data obtained in the thorough study of the hydroamination of activated alkenes catalyzed by the homoleptic complexes $[\{Ae[N(SiMe_3)_2]_2\}_2]$ (Ae = Mg, Ca, Sr, Ba) and $[Ae\{CH(SiMe_3)_2\}_2(THF)_2]$ (Ae = Ca, Sr) demonstrated that the Sr complex was indeed superior to that of Ca, and the Mg and Ba derivatives displayed very poor activities.[14–15] Unfortunately, no experimental data were available for the series of heteroleptic complexes $[\{L^3\}AeN(SiMe_3)_2(THF)_n]$, as the Sr and Ba species are not stable in solution.[10b]

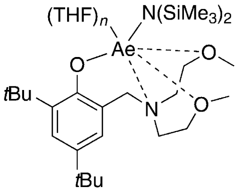
As part of our ongoing program aimed at implementing Ae-based catalysts for a diversity of transformations,[16] we report herein the use of three families of heteroleptic complexes of the large Ae metals supported by various ancillary ligands for the anti-Markovnikov intermolecular hydroamination of vinyl arenes and isoprene. In all cases, the activity trend varies in the order (Mg <)Ca < Sr < Ba, that is, the activity increases linearly with the size of the metal. Also, the catalytic activity in the intermolecular hydrophosphination of styrene follows the same order. The Ba complexes are not only the most active in these series, but also represent the first examples of complexes of this metal that are capable of promoting the intermolecular hydrofunctionalizations of alkenes.

The new heteroleptic complexes $[\{L^1\}AeN(SiMe_3)_2(THF)_n]$ [Ae = Ca ($n = 1$, **1**); Sr ($n = 2$, **2**); Ba ($n = 2$, **3**)], supported by the congested imino anilide ligand $\{L^1\}^-$,[17] were isolated in 45–70 % yields after the one-pot reaction of $\{L^1\}H$, AeI_2, and 2 equivalents of $KN(SiMe_3)_2$.[9] The final products showed no sign of contamination by homoleptic compounds and proved stable in C_6D_6 solutions up to 60 °C, as no evidence for ligand redistribution reactions could be detected.

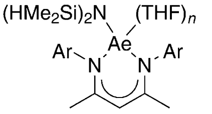


Ar = 2,6-*i*Pr$_2$-C$_6$H$_3$

Ae = Ca $n = 1$ (**1**)
Ae = Sr $n = 2$ (**2**)
Ae = Ba $n = 2$ (**3**)



Ae = Mg $n = 0$ (**4**)
Ae = Ca $n = 0$ (**5**)
Ae = Sr $n = 1$ (**6**)
Ae = Ba $n = 0$ (**7**)



Ar = 2,6-*i*Pr$_2$-C$_6$H$_3$

Ae = Ca $n = 1$ (**8**)
Ae = Sr $n = 2$ (**9**)
Ae = Ba $n = 2$ (**10**)

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[**] Financial support by the European Research Council (grant FP7-People-2010-IIF, *ChemCatSusDe*) is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201200364.

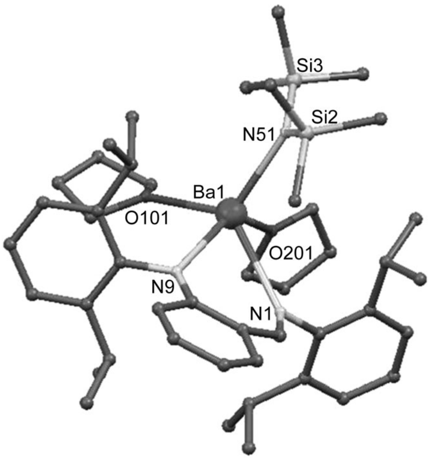


Figure 1. Representation of the molecular solid-state structure of $[\{L^1\}BaN(SiMe_3)_2(THF)_2]$ (**3**). Only the main sites are drawn for the disordered THF molecule (O(101)). Hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ba(1)–N(51) 2.623(3), Ba(1)–N(9) 2.677(2), Ba(1)–O(201) 2.766(2), Ba(1)–O(101) 2.810(3), Ba(1)–N(1) 2.825(3), Ba(1)–Si(1) 3.676(1), Ba(1)–Si(2) 3.758(1); Ba(1)-N(51)-Si(2) 119.78(14), Ba(1)-N(51)-Si(3) 114.85(15), N(1)-Ba(1)-N(9) 65.99(8).

The molecular structure of the five-coordinated complex **3** was obtained and is depicted in Figure 1. The Ba atom is located 1.14 Å above the mean plane formed by the NCCCN core, and accordingly the bite angle N(1)-Ba(1)-N(9) is very narrow (65.99°). The new, stable complexes $[\{L^2\}AeN(SiMe_3)_2(THF)_n]$ [Ae = Mg ($n = 0$, **4**); Sr ($n = 1$, **6**)], which incorporate the tetradentate amino-ether phenolate ligand $\{L^2\}^-$,[18] were synthesized following procedures already developed to obtain their Ca ($n = 0$, **5**)[16d] and Ba ($n = 0$, **7**)[16e] analogues. Inspired by the pioneering work by Anwander and co-workers with rare-earth metals,[19] we have recently shown that internal Ae···H–Si agostic interactions help stabilize heteroleptic Ae complexes against Schlenk-type equilibria.[16c–f] Exploiting this strategy that relies on the use of the $N(SiMe_2H)_2^-$ amido group, we have now prepared cleanly and in good yields (74–78%) the complexes $[\{L^3\}AeN(SiMe_2H)_2(THF)_n]$ [Ae = Ca ($n = 1$, **8**); Sr ($n = 2$, **9**); Ba ($n = 2$, **10**)] bearing the ubiquitous β-diketiminate ligand $\{L^3\}^-$. Until now, available synthetic heteroleptic Ae precursors containing this ancillary ligand were confined to $[\{L^3\}MgN(SiMe_3)_2]$ (and its alkyl/alkoxide derivatives)[20] and $[\{L^3\}CaN(SiMe_3)_2(THF)]$.[9,10b,11] The Sr and Ba congeners could be prepared but were prone to ligand scrambling, which hampered the synthesis of pure compounds.[10b]

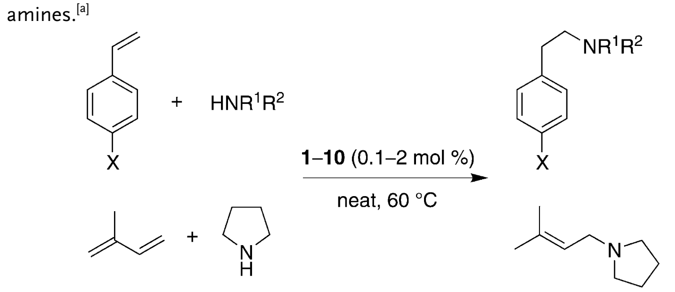
The ability of the new heteroleptic complexes **1**–**3** to catalyze the intermolecular hydrofunctionalization of activated alkenes was interrogated (Table 1). A moderate catalyst loading of 2 mol% in neat substrate was typically used at 60 °C. Much to our delight, **1**–**3** promoted the hydroamination of styrene with benzylamine, but contrary to expectations,[14,15] we found that the performance improved substantially and regularly from Ca to Ba. Wherein the Ba complex **3** achieved near-complete conversion within 18.5 hours (entry 4), the Ca (**1**) and Sr (**2**) complexes converted 34 and 71%, respectively, of the substrates (entries 1 and 2). Intrigued by this phenomenon, the families of complexes **4**–**7** (entries 5–8) and **8**–**10** (entries 9–11) were also tested under rigorously identical reaction conditions. In all cases, the trend (Mg $\ll$)Ca < Sr < Ba was obtained, that is, irrelevant of the identity of the ligand, the catalytic activity increased with the size of the metal. In agreement with the proposed theoretical models[14] and experimental observations,[3d,14,15] the reaction was fully regioselective, as the *anti*-Markovnikov product of addition to the alkene was always exclusively formed. Note that for any given metal, maximal activity was achieved with the ligand $\{L^3\}^-$, whereas the lowest conversions were recorded with the phenolate $\{L^2\}^-$ ligand (compare entries 1, 6, and 9; 2, 7, and 10; 4, 8, and 11). This data confirmed the superiority of the β-diketiminate over other ligand frameworks as is often observed for a number of reactions catalyzed by divalent metals. However, complexes **1**–**3** are more readily synthesized than **8**–**10** and displayed only slightly lower efficiency. Thus, the most active catalyst in this family, the Ba derivative **3**, was selected for subsequent investigations. The role of the identity of the amide moiety in the catalyzed reaction was negligible, as control experiments demonstrated that the activities of $[\{L^3\}CaN(SiMe_3)_2(THF)]$ and $[\{L^2\}BaN(SiMe_2H)_2]$[16e] matched those of **8** and **7**, respectively.[21]

The presence of an electron-donating substituent on the aromatic ring in vinyl arenes led to a marked decrease in catalyst activity (entries 4, 19, and 20), which is consistent with earlier results with Ae[3d,14] and rare-earth metals.[8] In our case, the presence of a chlorine atom did not lead to improved activity either (entry 21). The hydroamination of styrene with *n*-hexylamine also occurred fairly rapidly (entry 13), but the reaction was obviously sensitive to steric factors (entry 12).

The fastest reaction rates were achieved with pyrrolidine, as conversion of 50 equivalents was complete within 1 hour (entry 14). With [styrene]/[pyrrolidine]/[**3**] = 500:500:1 (entry 15) and 1000:1000:1 (entry 18), 85 and 58% conversions,respectively, were achieved within 2 hours with corresponding turnover frequencies (TOFs) of 212 and 290 h^{-1}. These values, which were achieved under mild reaction conditions, exceed those reported to date for intermolecular hydroamination reactions catalyzed by Ae,[3d,14,15] rare-earth,[8] or even late-transition-metal[22] complexes by one to two orders of magnitude. Notably, under identical reaction conditions, the best[15] bis(amide)s $[\{Ae[N(SiMe_3)_2]_2(THF)_2\}_2]$ (Ae = Ca, entry 16; Sr, entry 17), and homoleptic complexes recently reported[23] displayed vastly lower reaction rates. The selection of alkene was not restricted to vinyl arenes, as **3** catalyzed the reaction of isoprene and pyrrolidine with equal competence (entries 22 and 23). Full conversion was observed within 1 hour using 2 mol% of **3**, and gratifyingly the conversion reached 59% after 2 hours (TOF = 295 h^{-1}) when as little as 0.1 mol% of **3** was employed. The reaction was 1,4-regioselective, with anti-Markovnikov addition of pyrrolidine occurring exclusively on the least encumbered unsaturation to give 1-(3-methylbut-2-en-1-yl)pyrrolidine.

Kinetic studies of the hydroamination of styrene with pyrrolidine catalyzed by **3** were performed under a broad range of amine, styrene, and catalyst concentrations by using

Table 1: Ae-catalyzed intermolecular hydroamination of activated alkenes with amines.[a]



Entry	Catalyst	Substrate	Amine	t [h]	Conv. [%][b]
1	**1**	styrene (X = H)	$BnNH_2$	18.5	34
2	**2**	styrene	$BnNH_2$	18.5	71
3	**3**	styrene	$BnNH_2$	2	42
4	**3**	styrene	$BnNH_2$	18.5	86
5	**4**	styrene	$BnNH_2$	18.5	1
6	**5**	styrene	$BnNH_2$	18.5	6
7	**6**	styrene	$BnNH_2$	18.5	24
8	**7**	styrene	$BnNH_2$	18.5	37
9	**8**	styrene	$BnNH_2$	2	29
10	**9**	styrene	$BnNH_2$	2	42
11	**10**	styrene	$BnNH_2$	2	64
12	**3**	styrene	$i\mathrm{Pr}_2NH$	18.5	0
13	**3**	styrene	$n\mathrm{Hex}NH_2$	18.5	55
14	**3**	styrene	$(CH_2)_4NH$	1	99
15[c]	**3**	styrene	$(CH_2)_4NH$	2	85
16[c]	$[Ca[N(SiMe_3)_2]_2(THF)_2]$	styrene	$(CH_2)_4NH$	2	< 1
17[c]	$[Sr[N(SiMe_3)_2]_2(THF)_2]$	styrene	$(CH_2)_4NH$	2	10
18[d]	**3**	styrene	$(CH_2)_4NH$	2	58
19	**3**	styrene (X = Me)	$BnNH_2$	18.5	41
20	**3**	styrene (X = OMe)	$BnNH_2$	18.5	11
21	**3**	styrene (X = Cl)	$BnNH_2$	18.5	65
22[e]	**3**	isoprene	$(CH_2)_4NH$	1	99[f]
23[g]	**3**	isoprene	$(CH_2)_4NH$	2	59[f]

[a] Reaction conditions: [alkene]/[amine]/[catalyst] = 50:50:1 unless otherwise specified, 10.5 μmol of catalyst, no additional solvent, $T = 60\,^\circ C$. [b] Determined by ^1H NMR spectroscopy. [c] [styrene]/[pyrrolidine]/[**3**] = 500:500:1. [d] [styrene]/[pyrrolidine]/[**3**] = 1000:1000:1. [e] [isoprene]/[pyrrolidine]/[**3**] = 220:50:1. [f] Based on amine conversion. [g] [isoprene]/[pyrrolidine]/[**3**] = 2000:1000:1.

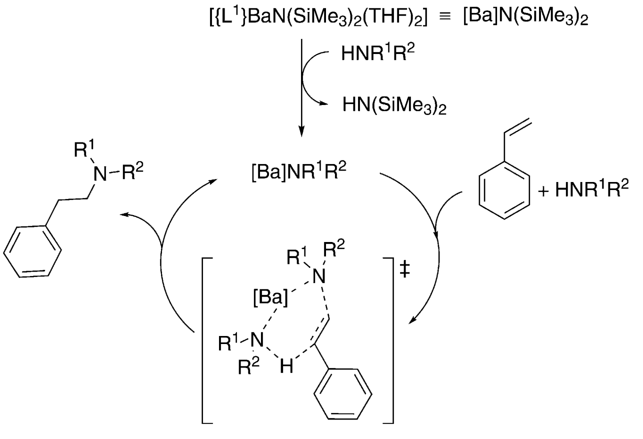
^1H NMR spectroscopy.[21] The determined empirical rate law [Eq. (1)],

$$v = k[\text{styrene}]^{1.0}[\text{pyrrolidine}]^{1.0}[\mathbf{3}]^{1.0} \qquad (1)$$

with partial first order in each of the components of the system, differs from that established for rare-earth catalysts: Marks and co-workers showed that the kinetics of the hydroamination of alkynes with primary amines were zero order in amine and first order in catalyst and alkyne concentrations.[8,24] The activation parameters for **3**, $E_a = 19.0(0.6)\ \mathrm{kcal\,mol^{-1}}$, $\Delta H^{\neq} = 18.3(0.8)\ \mathrm{kcal\,mol^{-1}}$, and $\Delta S^{\neq} = -13.1(2.7)\ \mathrm{cal\,mol^{-1}\,K^{-1}}$, were extracted by Arrhenius and Eyring analyses of the kinetic data obtained in the temperature range 25–60 °C. These values are diagnostic of ordered transition states. The calculated $\Delta G^{\neq}$ for this process at 298 K is 22.4 $\mathrm{kcal\,mol^{-1}}$, which compares favorably with the values reported for $[\{Ca[N(SiMe_3)_2]_2\}_2]$ (24.1 $\mathrm{kcal\,mol^{-1}}$) and $[\{Sr[N(SiMe_3)_2]_2\}_2]$ (23.4 $\mathrm{kcal\,mol^{-1}}$) for the catalyzed hydroamination of styrene with piperidine.[14–15]

The rate law featured in the case of **3** points to a different mechanism from that proposed for rare-earth systems, or at least one wherein the rate-limiting step is not the intermolecular insertion of the alkene into the Ba−N(pyrrolidine) bond. A plausible mechanism compatible with Equation (1) involves a one-step, non-insertive route with a six-centered transition state (Scheme 1). It proceeds through a concerted proton transfer onto the unsaturation activated towards the attack of the nucleophile. This hypothesis, where the N−H bond plays a key role in the transition state, is corroborated by the strong kinetic isotope effect (KIE) observed during the monitoring of the reaction of styrene with deuterated pyrrolidine catalyzed by **3**: k_H/k_D ratios of 6.8 and 7.3 were found at 40 and 60 °C, respectively.[21] These values are intermediary between the theoretical maximum of 8.5[25] or the ratio reported for $[\{Sr[N(SiMe_3)_2]_2\}_2]$ ($k_H/k_D = 7.9$ at 55 °C), and the values found for $[\{Ca[N(SiMe_3)_2]_2\}_2]$ ($k_H/k_D = 4.3$ and 4.1 at 70 °C and 55 °C respectively)[15] or $[(C_5Me_5)_2LaCH(SiMe_3)_2]$ ($k_H/k_D = 4.1$ at 25 °C).[26] Note that a related mechanism has been debated for the intramolecular cyclohydroamination of aminoalkenes with a Mg complex,[3b,c] and a mechanism reported during submission of this manuscript by Hill and co-workers for intermolecular reactions catalyzed by homoleptic complexes also bears strong analogy.[15]

Complexes **1**–**3**, **5**–**7**, and **8**–**10** also all catalyzed the intermolecular hydrophosphination of styrene with $HPCy_2$ or $HPPh_2$ (catalyst loading 2 mol %, 60 °C, neat). Here also, the activity trend was Ca < Sr < Ba, although the performances now increased according to $\{L^3\}^- < \{L^1\}^- \approx \{L^2\}^-$.[21] The reactions proceeded with perfect anti-Markovnikov regioselectivity. With $HPCy_2$, only partial conversion was achieved after 18.5 hours, even with **1**–**3**, the most active complexes for this transformation (ca. 42 % with **3**). In contrast, the reactions with the less basic $HPPh_2$ were considerably faster, and 96 % conversion was achieved using **3** in as little as 15 minutes. The corresponding TOF



Scheme 1. Possible six-centered concerted mechanistic pathway for styrene/amine intermolecular hydroamination catalyzed by **3**.

(192 h^{-1}) outclasses that reported with $[\{L^3\}CaN(SiMe_3)_2(THF)]$ (ca. 0.5 h^{-1} at 75 °C),[12a] whereas rare-earth complexes are not known to catalyze this reaction.

In conclusion, several complete families of stable complexes of the large Ae metals which catalyze intermolecular hydrofunctionalization reactions of activated alkenes have been prepared. Contrary to expectations based on previous computations, it was found that the catalyst activity increased systematically with the size of the metal, and the barium complexes have, for the first time, displayed impressive efficacy in these catalytic reactions. In particular, the stable and readily accessed imino anilide barium complex $[\{L^1\}BaN(SiMe_3)_2(THF)_2]$ (**3**) offers real potential as catalyst for a variety of organic transformations. We are now exploring this avenue and further studies are also underway to assess the validity of the proposed mechanism.

Experimental Section

Details for the syntheses and characterization of compounds **1**–**10** and experimental protocols for catalytic tests are given in the Supporting Information.

Received: January 13, 2012
Revised: February 17, 2012

Keywords: alkaline-earth metals · barium · homogeneous catalysis · hydroamination · ligand design

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Communications

Synthetic Methods

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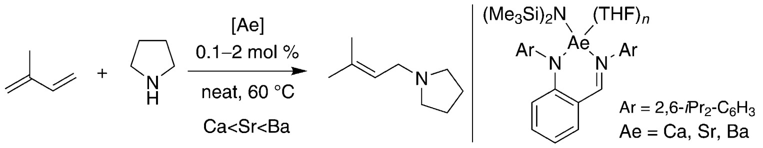
When Bigger Is Better: Intermolecular Hydrofunctionalizations of Activated Alkenes Catalyzed by Heteroleptic Alkaline Earth Complexes



New alkaline-earth amido complexes catalyze the regioselective intermolecular hydroamination (see scheme; Ae = alkaline earth) and hydrophosphination of styrene and isoprene with unprecedented activities. The catalytic performances increased linearly with the size of the metal.