Heterobimetallic Catalysis

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Assembling Zirconium and Calcium Moieties through an Oxygen Center for an Intramolecular Hydroamination Reaction: A Single System for Double Activation**

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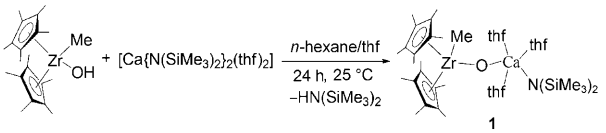
Dedicated to Prof. Dr. Didier Astruc on the occasion of his 65th birthday

The catalytic addition of a N–H bond across a C–C multiple bond (hydroamination) offers an efficient and atom-economical route to produce nitrogen-containing molecules, which are of great interest to academic and industrial researchers.[1] Over the last decade, there have been enormous efforts to develop an efficient catalyst for this demanding transformation. The most recent trend has been the use of catalysts that involve Group 2 metals, which show high catalytic conversion for intramolecular hydroamination reactions under relatively mild reaction conditions.[2] Moreover, catalysts based on Group 4 metals have traditionally shown very high activity in the hydroamination catalysis, as reported by Schafer and others.[3,4] However, no studies have ever considered the activation of aminoalkenes by a catalytic system that combines Group 2 and Group 4 metals. Two metal centers with entirely different chemical properties have attracted chemists for a long time, not only from the point of synthetic challenge, but also from their cooperative activity.[5] In this area, one of the major challenges has been the development of a system in which two metal centers will act catalytically in different manners. Heterobimetallic complexes in general have enormous potential to revolutionize homogeneous catalytic processes.[5] Recently, we have demonstrated a new synthetic route by which a plethora of heterometals can be assembled through an oxygen atom.[6] The synthetic strategy takes advantage of unprecedented syntheses of a number of well-defined hydroxide precursors of the type LMR(OH) (M = Al, Ga, or Ge; R = alkyl, aryl, or electron lone pair; L = $CH\{N(Ar)(CMe)\}_2$ with Ar = 2,6-iPr$_2$C$_6$H$_3$), $[LSr(\mu\text{-}OH)]_2\cdot(thf)_3$, and $[Cp^*_2(Me)Zr(OH)]$ ($Cp^* = C_5Me_5$).[6–8] This synthetic development resulted in the access of a new class of catalysts bearing enhanced Lewis acidic metal centers through oxygen bridging.[6]

Herein we show for the first time that a Group 4 metal can be fixed on a Group 2 metal through an oxygen bridge to carry out intramolecular hydroamination of primary and secondary aminoalkenes. In this study we have synthesized a Zr-O-Ca-based heterobimetallic compound $[Cp^*_2(Me)Zr(\mu\text{-}O)Ca(thf)_3\{N(SiMe_3)_2\}]$ (**1**). We investigated the catalytic properties of **1** for intramolecular hydroamination reactions of primary and secondary aminoalkenes.

Synthesis of **1** was accomplished by reacting the monometallic hydroxide precursor $[Cp^*_2(Me)Zr(OH)]$ with $[Ca\{N(SiMe_3)_2\}_2\cdot(thf)_2]$ under elimination of $HN(SiMe_3)_2$ (Scheme 1). A solution of $[Cp^*_2(Me)Zr(OH)]$ in *n*-hexane/THF (2:1 ratio) was added drop by drop to the solution of $[Ca\{N(SiMe_3)_2\}_2\cdot(thf)_2]$ in a 1:1 stoichiometric ratio in *n*-hexane at 0 °C and stirred at 25 °C for 24 h to yield **1**. Compound **1** is insoluble in *n*-pentane but readily dissolves in toluene and THF, and it was characterized by ^{1}H, ^{13}C, ^{29}Si NMR spectroscopy, EI mass spectrometry, and single-crystal X-ray diffraction studies.



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Scheme 1. Synthesis of complex **1**.

The ^{1}H NMR spectrum of **1** in C_6D_6 exhibits three singlets at $\delta = -0.36$, 0.51, and 1.90 ppm, which are attributed to the proton resonances arising from Zr–Me, $N(SiMe_3)_2$, and η^5-C_5Me_5 groups, respectively. The Zr–Me proton resonance is shifted upfield to $\delta = -0.36$ ppm in **1** relative to that observed for $[Cp^*_2(Me)Zr(OH)]$ ($\delta = -0.2$ ppm),[9a] whereas the Ca–$N(SiMe_3)_2$ proton resonance of **1** ($\delta = 0.51$ ppm) is shifted downfield when compared with that observed for the starting

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material $[Ca\{N(SiMe_3)_2\}_2(thf)_2]$ ($\delta = 0.38$ ppm).[9b] The ^{13}C NMR spectrum of **1** reveals a resonance at $\delta = 22.7$ ppm, which is assigned to the zirconium-bound methyl carbon atom. The ^{29}Si NMR spectrum exhibits a resonance at $\delta = -13.5$ ppm arising from the silicon nucleus of the $N(SiMe_3)_2$ group.

Analytically pure crystals of **1** were obtained from a cold toluene/THF solution (3:1 ratio) at 0°C, and finally the structure of **1** was determined by single-crystal X-ray crystallography (Figure 1).[10] Compound **1** crystallizes in the

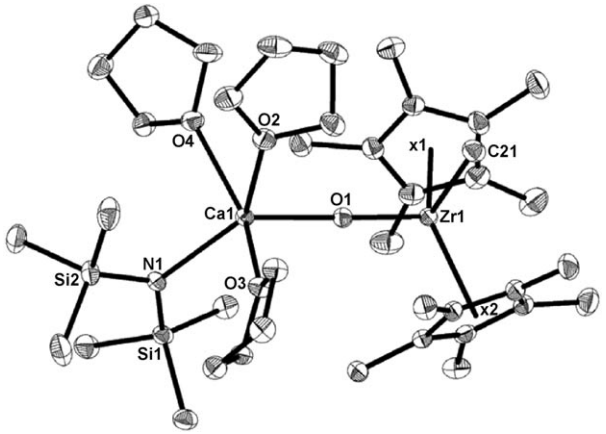


Figure 1. View of the molecular structure of **1**. Ellipsoids are set at 50% probability; hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and angles [°]: Ca1–O1 2.2068(13), Ca1–O2 2.4165(14), Ca1–O3 2.4357(13), Ca1–N1 2.3706(16), Zr1–C21 2.326(2), Zr1–O1 1.8879(13); Ca1-O1-Zr1 176.98(7), O1-Ca1-N1 126.27(5). x = centroid of Cp* ring.

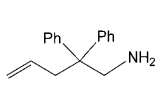
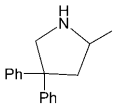
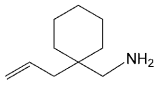
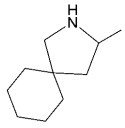
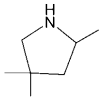
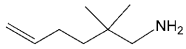
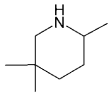
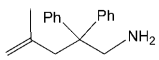
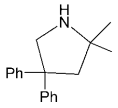
monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit. The X-ray structural analysis of **1** reveals that the calcium atom is bonded through a bridging oxygen atom to the zirconium center. The calcium atom is surrounded by four oxygen atoms (one bridging oxygen atom and three oxygen atoms from THF molecules) and a nitrogen atom of the amide group. The calcium center adopts a distorted trigonal bipyramidal geometry, whereas the geometry around the zirconium center is distorted-tetrahedral, considering η^5-C_5Me_5 as single coordination site. The Ca1–N1 bond distance (2.3706(16) Å) is comparable to that found in $[LCa\{N(SiMe_3)_2\}(thf)]$ ($L = CH\{N(Ar)(CMe)\}_2$, $Ar = 2,6\text{-}iPr_2C_6H_3$; 2.313 Å).[11a] The bond angle of Ca-O-Zr is nearly linear (ca. 177°) and is wider than the previously observed bond angles in related heterobimetallic complexes $[Cp^*_2(Me)Zr(\mu\text{-}O)Ti(NMe_2)_3]$ (Zr-O-Ti = 169.7°) and $[Cp^*_2(Me)Zr(\mu\text{-}O)Hf(NMe_2)_2(\mu\text{-}O)Zr(Me)Cp^*_2]$ (Zr-O-Hf = 169.4°),[11b] reflecting a higher steric demand in case of compound **1** (see the Supporting Information).

The increasing demand to develop an efficient catalyst for the hydroamination reaction prompted us to test the catalytic activity of complex **1** towards intramolecular hydroamination. A previous study by Scott and co-workers has demonstrated that the zirconium alkyl cation catalyzes the cyclization of secondary aminoalkenes.[4a] Recent developments established that divalent Group 2 metal complexes, such as β-diketiminatocalcium bis(trimethylsilyl)amide $[LCa\{N(SiMe_3)_2\}(thf)]$ ($L = CH\{N(Ar)(CMe)\}_2$, $Ar = 2,6\text{-}iPr_2C_6H_3$), can activate primary aminoalkenes.[2g] The successful synthesis of complex **1** in which a tetravalent Group 4 metal fragment, such as methyl zirconocene, and a divalent Group 2 metal, such as calcium, are assembled through an oxygen center gave us a unique opportunity to check its efficiency towards catalytic activation of primary and secondary aminoalkenes. Thus our aim has been to use the single well-defined heterobimetallic complex **1** for the activation of primary and secondary aminoalkenes.

The study started with unactivated primary aminoalkenes. The reaction of catalyst **1** with dry, degassed aminoalkenes proceeds regiospecifically, and the primary aminoalkenes were converted almost quantitatively to the cyclic product under mild reaction conditions (25–80°C). The results of catalyst **1** with different primary aminoalkenes are summarized in Table 1. The progress of the hydroamination reaction of the primary aminoalkene (1-allylcyclohexyl)methylamine (**2**; substrate of Table 1, entry 2) to the corresponding cyclic product using catalyst **1** was monitored by in situ ^1H NMR spectroscopic studies (see the Supporting Information).

The presence of the methyl zirconocene moiety in compound **1** motivated us to test its efficacy in the activation of secondary aminoalkenes, as methyl zirconocene has been found to activate the secondary aminoalkenes in the presence of an externally added activator.[4b] At first, we carried out the

Table 1: Intramolecular hydroamination of unactivated primary aminoalkenes using catalyst **1**.[a]

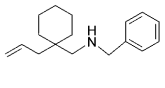
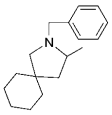
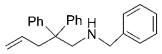
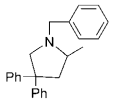
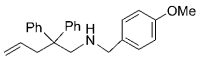
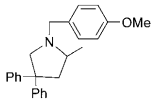
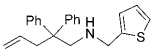
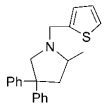
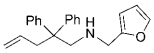
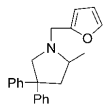
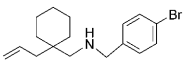
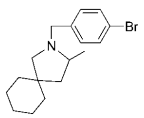
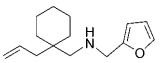
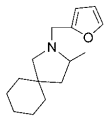
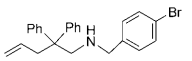
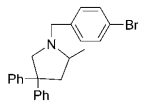
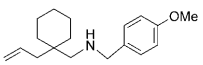
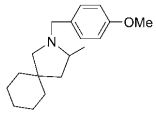
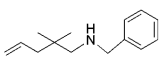
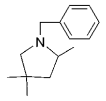
Entry	Substrate	Product	*t* [h]	Conversion [%][b]
1			8.6	98,[c] [92][d]
2			12	96,[c] [87][d]
	2		8	99[e]
3			45	80[f]
4			30	92[g]
5			20	98[h]

[a] Reaction conditions: amine (30 μL) in 0.6 mL C_6D_6. [b] Determined by ^1H NMR spectroscopy against an internal standard. [c] Reaction carried out with 10 mol% catalyst loading at 25°C. [d] Yield of isolated product. [e] Conversion determined by ^1H NMR spectroscopy using related oxygen-bridged bimetallic calcium amido catalyst $[\{(iPrAT)Ca\{N(SiMe_3)_2\}(thf)\}_2]$ (*i*PrAT = 2-(isopropylamino)troponate) for substrate **2**.[12] [f] Reaction carried out with 10 mol% catalyst loading at 80°C. [g] Reaction carried out with 20 mol% catalyst loading at 80°C. [h] Reaction carried out with 13 mol% catalyst loading at 80°C.

catalytic hydroamination reaction of (1-allylcyclohexylmethyl)benzylamine (substrate of Table 2, entry 1) with **1** in C_6D_6, maintaining the bath temperature at 110 °C without adding any activator. After 20 h of heating we found less than 10 % conversion to the hydroamination product. To increase the catalytic activity of **1** for secondary aminoalkenes, we performed the reaction with an equimolar amount of the activator $[PhNMe_2H][B(C_6F_5)_4]$ (with respect to the catalyst) and we found that after 20 h at 110 °C in C_6D_6, the conversion was 99 % (Table 2, entry 1). This fact may be attributed to the generation of the in situ cationic zirconium species where the activator acts as a methyl abstracting reagent. The activator, $[PhNMe_2H][B(C_6F_5)_4]$, has been used previously to generate a cationic zirconium species through abstraction of a methyl moiety.[4b] To check the generality of the catalytic activity of **1** on secondary aminoalkenes, we investigated the reaction with a number of secondary aminoalkenes in the presence of the activator at 110 °C in C_6D_6 (Table 2) revealing very high catalytic conversion of a range of secondary aminoalkenes to the corresponding cyclic products. The catalytic activity of **1** compares well with that observed for alkyl zirconium catalyst for a range of other secondary aminoalkenes.[4a]

We carried out detailed kinetic studies to gain further insight into the catalytic process of **1** using the primary and secondary aminoalkenes in C_6D_6. A plot of $\ln(C/C_0)$ for **2** versus time provides a straight line with negative slope (Figure 2a), revealing an overall first order rate for the reaction. A detailed kinetic study reveals the first-order rate dependence on catalyst concentration (see the Supporting Information). The first-order rate of the reaction with respect to the catalyst concentration was further confirmed from van't Hoff plot. A plot of $\ln k_{obs}$ versus the natural logarithm of the catalyst concentration provides a straight line (Figure 2b) with a slope of 1.04 (where the slope corresponds to the reaction rate). To gain a preliminary understanding of the mechanistic pathway of the cyclization process, we carried out an H/D kinetic isotope effect (KIE) experiment under the reaction conditions using **2** and $[D_2]$**2**. The experiment resulted in a substantial KIE of 2.42 (Figure 2a, see also the Supporting Information). This observation suggests that a hydrogen of the amino group of **2** is involved in the key step of the primary aminoalkene activation process. Similarly, we carried out the kinetic study for cyclization of (1-allylcyclohexylmethyl)benzylamine (substrate of Table 2, entry 1) using catalyst **1**. In this case we also found that the overall

Table 2: Intramolecular hydroamination of unactivated secondary aminoalkenes using catalyst **1**.[a]

Entry	Substrate	Product	*t* [h]	Conversion [%][b]
1			20	99
2			20	98
3			50	99
4			30	96, [90][c]
5			30	99, [93][c]
6			48	99
7			36	99
8			50	98
9			24	99
10			48	69

[a] Reaction conditions: amine (30 μL), catalyst (10 mol %), $[PhNMe_2H][B(C_6F_5)_4]$ (10 mol %) in 0.6 mL C_6D_6 at 110 °C. [b] Determined by ^{1}H NMR spectroscopy against an internal standard. [c] Yield of isolated product.

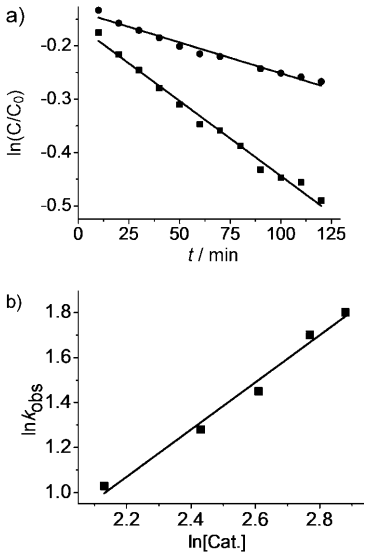


Figure 2. a) Plot of $\ln(C/C_0)$ versus time for the cyclization of **2** (■; substrate of Table 1, entry 2) and $[D_2]$**2** (●) catalyzed by **1** in C_6D_6 at 25 °C. For $[D_2]$**2**: $y = -0.00116x - 0.13541$, $R^2 = 0.97333$; For **2**: $y = -0.00281x - 0.16261$, $R^2 = 0.98849$. b) Plot of $\ln k_{obs}$ versus ln[Cat.] for the cyclization of **2** by **1** in C_6D_6 at 25 °C (van't Hoff plot). $y = 1.04811x - 1.23556$, $R^2 = 0.98007$.

reaction rate was first-order and the reaction rate depends directly on the catalyst concentration (see the Supporting Information).

Preliminary investigations into the cyclization process of primary aminoalkenes indicate that the activation of primary aminoalkenes occurs by the amine activation pathway. The ^{1}H NMR spectrum of the reaction mixture exhibits the formation of free $HN(SiMe_3)_2$ (at $\delta = 0.1$ ppm), indicating involvement of the calcium center during the catalytic cycle. This fact is also supported by the substantial kinetic isotope effect (KIE of 2.42), which suggests that amine activation is one of the most important steps during the catalytic cycle. The amine activation pathway has been established previously using a calcium-based catalyst for primary aminoalkenes.[2d,g] Moreover, the proton resonances arising from the Zr–Me group and from the zirconium bound Cp* groups do not undergo any significant changes during the activation of the primary aminoalkenes. This result indicates that the zirconium center does not participate in the activation process. However, in the case of secondary aminoalkenes, we found that after the addition of an equimolar amount of the activator (with respect to the catalyst), the Zr–Me resonance ($\delta = -0.36$ ppm) vanishes completely. We have calculated the feasibility of the formation of cations at the zirconium site as well as at the calcium center with the help of density functional theory (DFT; see the Supporting Information). The calculations reveal that the Gibbs free energy change (ΔG) at 298 K is favorable for the formation of a cation at the zirconium center, whereas the formation of a cation at the calcium center is not energetically feasible after treatment with the activating agent. The ΔG values are -15.9 kcal mol^{-1} and 12.5 kcal mol^{-1} for generation of a cation at the zirconium center and at the calcium center, respectively. This result clearly supports the proposal that the formation of a cation at the zirconium center is energetically and thermodynamically more feasible. This observation supports the hypothesis that the secondary aminoalkenes form cyclic products via an activation pathway through the zirconium center, an observation previously accomplished in a different alkyl zirconium-based catalyst with secondary aminoalkenes.[4]

In summary, for the first time, a transition metal can be fixed on a main-group alkaline earth metal through an oxygen bridge, and we show that combining Group 2 and 4 metals into a single system can lead to the activation of both primary and secondary aminoalkenes. The synthesis of the heterobimetallic complex $[Cp^*_2(Me)Zr(\mu\text{-}O)Ca(thf)_3\{N(SiMe_3)_2\}]$ (**1**) containing a tetravalent Group 4 metal and a divalent Group 2 metal bridged by an oxygen center was accomplished by the reaction of $[Cp^*_2(Me)Zr(OH)]$ with $[Ca\{N(SiMe_3)_2\}_2\cdot(thf)_2]$ at room temperature under elimination of $HN(SiMe_3)_2$. We have demonstrated that the two different catalytically active metal centers present in compound **1** can be used to activate the primary and secondary aminoalkenes. A number of primary and secondary aminoalkenes was successfully converted to cyclic products using the catalyst **1**. Preliminary investigation indicates that the calcium center activates the primary aminoalkenes and the zirconium center activates the secondary aminoalkenes. This work represents a major step forward in the development of heterobimetallic catalysis for the intramolecular hydroamination of primary and secondary aminoalkenes through a single catalytic system.

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[10] Crystal data for **1**: $C_{39}H_{75}CaNO_4Si_2Zr$, $M_r = 809.48$, $0.4 \times 0.26 \times 0.2\ mm^3$, monoclinic, space group $P2_1/n$, $a = 14.4608(12)$, $b = 9.4611(16)$, $c = 16.7106(15)$ Å, $\beta = 109.4660(10)°$, $V = 4.4339(7)\ nm^3$, $Z = 4$, $\rho_{calc} = 1.213\ Mg\,m^{-3}$, $\mu\ (Mo_{K\alpha}) = 0.453\ mm^{-1}$, $T = 100(2)$ K, θ range for data collection = 3.02–26.03°, 37016 reflections measured, 8592 independent ($R_{int} = 0.0355$), $R_1 = 0.0306$ ($I > 2\sigma(I)$), $wR_2 = 0.071$(all data), residual density peaks 0.320 to $-0.320\ e\,Å^{-3}$. CCDC 801838 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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