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Communication

Intramolecular hydroamination catalysis using *trans*-*N*,*N*′-dibenzylcyclam zirconium complexes

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ABSTRACT

The syntheses of (Bn_2Cyclam)Zr(NMe_2)$_2$ (**1**), (Bn_2Cyclam)Zr($NH^{2,6\text{-}Me}$Ph)Cl (**2**) and (Bn_2Cyclam)Zr($N^{2,6\text{-}Me}$Ph) (**3**) are described. The reactivity of **1**, **3**, (Bn_2Cyclam)Zr(CH_2Ph)$_2$ (**4**) and (($C_6H_4CH_2$)$_2$Cyclam)Zr (**5**) as hydroamination catalysts of aminoalkenes is reported. High conversions of the primary *gem*-disubstituted aminoalkenes in 5- or 6-member ring N-heterocycles were observed. Reactions of **1**, **4** and **5** with CH_2=$CHCH_2CPh_2CH_2NH_2$ gave (Bn_2Cyclam)Zr(NHR)$_2$ (**6**) (R = $CH_2CPh_2CH_2CH$=CH_2) that on heating converts sequentially into the mono-*ortho*-metallated species (($C_6H_4CH_2$)BnCyclam)Zr(NHR) (**7**) and the bis-*ortho*-metallated (($C_6H_4CH_2$)$_2$Cyclam)Zr (**5**), simultaneously with the hydroamination product.

1. Introduction

Hydroamination is an atom-efficient procedure for the assembly of carbon–nitrogen bonds through the inter- or intramolecular addition of an amine to a carbon–carbon unsaturated bond [1]. Although enthalpically favoured, the negative entropy balance of the reaction requires that a catalyst activates the amine and/or the carbon–carbon bond for the coupling process [2].

Research on this topic showed that a wide variety of metal compounds along the Periodic Table are suitable catalysts for these transformations [1,3]. Although titanium derivatives proved extremely successful in the intermolecular alkyne hydroamination [4], expanding the general use of Group 4 metal compounds to intramolecular hydroamination processes was attained only recently. Cationic Zr and Ti complexes were found to catalyze the hydroamination of secondary aminoalkenes [5], while neutral Group 4 metal compounds were used for primary aminoalkenes and aminoalkynes [6]. Currently, intense research efforts are being made at the development of Group 4 metal complexes due to the fact they combine high activity and good selectivity (regio- and enantioselectivity) with chemical robustness.

In this contribution we present preliminary results on aminoalkene hydroamination using a new class of zirconium catalyst precursors supported by a dianionic *trans*-disubstituted cyclam ligand, Bn_2Cyclam. The flexibility of the ancillary ligand, already evidenced by its hemiliable behavior [7], as well as its participation in C–H activation reactions [8] are expected to play a prominent role in catalysis. We anticipate that these features are particularly relevant in processes that involve proton exchange as is the case of hydroamination.

2. Results and discussion

The synthetic routes for the preparation of (Bn_2Cyclam)Zr(NMe_2)$_2$ (**1**), (Bn_2Cyclam)Zr($NH^{2,6\text{-}Me}$Ph)Cl (**2**), (Bn_2Cyclam)Zr($N^{2,6\text{-}Me}$Ph) (**3**), (Bn_2Cyclam)Zr(CH_2Ph)$_2$ (**4**) and (($C_6H_4CH_2$)$_2$Cyclam)Zr (**5**) are presented in Scheme 1. Complex **1** was prepared by aminolysis of Zr(NMe_2)$_4$ with Bn_2Cyclam in 82% yield. **2** and **4** were prepared by chloride metathesis of (Bn_2Cyclam)ZrCl_2 [9] with $LiNH^{2,6\text{-}Me}$Ph and $MgClCH_2$Ph, respectively. Addition of MgClMe to compound **2** gave the imido derivative **3**, upon methane elimination in 68% yield. As reported previously, **5** can be obtained by heating solutions of the bis (alkyl) complex **4** [8].

In order to evaluate the behavior of different types of zirconium derivatives incorporating this macrocyclic ligand, complexes

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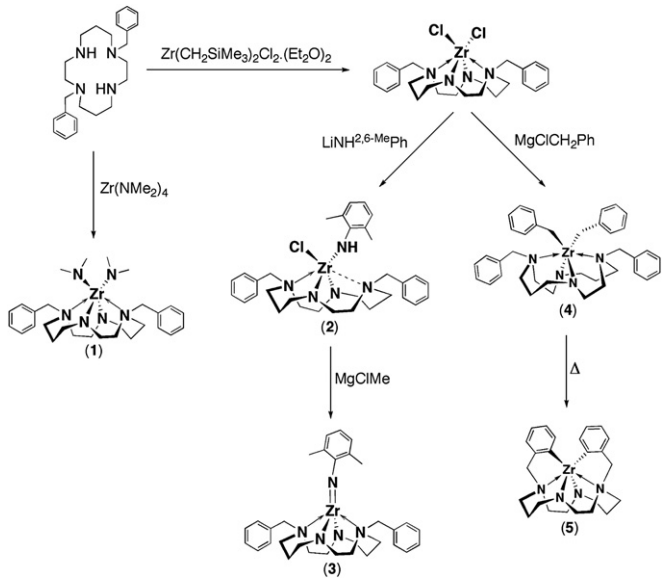
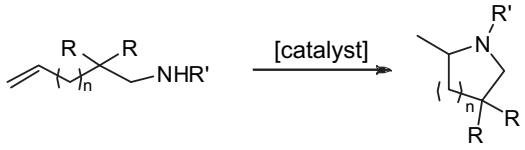


Scheme 1.

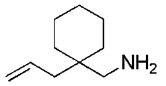
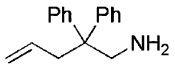
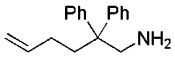
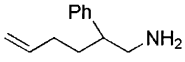
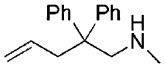
1, **3**, **4** and **5** were screened as aminoalkene hydroamination catalysts (Eq. 1). (1)



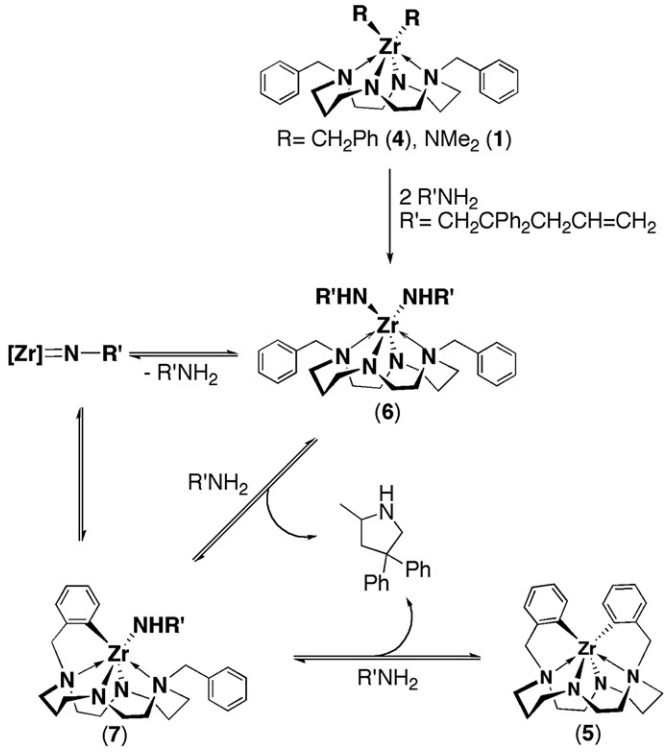
The results displayed in Table 1 show that all complexes are able to perform the intramolecular cyclization of primary aminoalkenes leading to the formation of five-member azacycles using a 10% catalyst load in toluene-d_8 at 115 °C.

Using *C*-(1-allyl-cyclohexyl)-methylamine as a reference substrate, the results show that complexes **1** and **4** are more active than **3** and **5**. Indeed, the conversion of *C*-(1-allyl-cyclohexyl)-methylamine and 2,2-diphenyl-pent-4-enylamine to the corresponding hydroamination products is quantitative after 3 h and 4.5 h, respectively, when **1** and **4** are used as catalyst precursors. It should be mentioned that regardless of the activity, all compounds reach quantitative substrate conversion and selectivity. **1** and **4** are also efficient catalysts for the cyclization of 2,2-diphenyl-hex-5-enylamine but neither of them react with 2-phenyl-hex-5-enylamine or 2,2-diphenyl-hex-5-enylmethylamine. The lack of reaction with 2-phenyl-hex-5-enylamine reveals the importance of the Thorpe-Ingold effect in intramolecular hydroamination [10]. On the other hand, the absence of reaction with secondary amines [11] is usually associated with the formation of terminal metal-imido moieties. The latter are thought to undergo a [2 + 2] cycloadition reaction to form an azametallacyclobutene intermediate and have been proposed as active species in Ti and Zr catalyzed hydroamination reactions [4e,4f,6j,12]. This type of mechanism does not seem to be in line with our previously described results on the reactivity of amido and imido complexes incorporating this macrocyclic ligand. We have shown that terminal imido compounds of general formula (Bn_2Cyclam)Zr=NR are not formed by amine elimination from (Bn_2Cyclam)Zr$(NHR)_2$ solutions [7] but require methane elimination from putative (Bn_2Cyclam)Zr(NHR)(CH_3), as described for the synthesis of **3**. Moreover, reactions of (Bn_2Cyclam)Zr($N^{2,6\text{-}iPr}$Ph) with acetylenes did not show any evidence for the formation of [2 + 2] addition products but followed decomposition pathways; exception was the reaction of the imido complex with phenylacetylene that led to (Bn_2Cyclam)Zr$(CCPh)_2$ and $^{2,6\text{-}iPr}PhNH_2$ [7]. Thus the lack of reactivity observed with secondary amines in our case may be due to the increased steric bulk of this amine substrate over its primary amine congener.

Table 1
Synthesis of cycloalkylamine derivatives via catalytic hydroamination.

Substrate	Catalyst	Time (h)	Conversion (%)
	1	3	> 98
	3	7	90
	4	3	> 98
	5	7	> 98
	1	4.5	> 98
	4	4.5	> 98
	5	6	90
	1	48	> 98
	4	48	> 98
	1	24	0
	4	24	0
	1	24	0
	4	24	0

Stoichiometric reactions of **1**, **4** and **5** with 2,2-diphenyl-pent-4-enylamine in benzene-d_6 were conducted and followed by NMR spectroscopy to gain insight into the mechanism of alkene hydroamination promoted by these compounds (Scheme 2).



Scheme 2.

The addition of two equivalents of aminoalkene to the solutions of **1** or **4**, at room temperature, led to the quantitative formation of (Bn_2Cyclam)Zr(NHR)$_2$ (R = $CH_2CPh_2CH_2CH{=}CH_2$) (**6**). Sequential addition of one plus one equivalents of 2,2-diphenyl-pent-4-enyl-amine to a solution of **5** gives the mono-*ortho*-metallated complex **7** and then the bis-amido **6**, in quantitative yield at room temperature. The formation of 2-methyl-4,4-diphenylpyrrolidine and **7** is observed when solutions of **6** are kept at room temperature for a few hours. Upon heating the solution until 90 °C, **6** is converted quantitatively to **7** and further heating of this solution gives **5** as the only zirconium complex.

Even though the NMR data do not reveal any terminal or bridging zirconium imido species or free amine, the occurrence of fast equilibria between **7** or **6** and (Bn_2Cyclam)Zr(NR) (Scheme 2) cannot be excluded [6m,13a–d]. Alternatively the cyclization reaction may occur through insertion of C=C in the Zr–NHR bond. This type of mechanism was proposed for the intramolecular hydroamination of aminoalkenes catalyzed by lanthanides and by constrained geometry zirconium and actinide complexes [6a, 6e, 14]. In this instance, the accessibility of the C=C to the metal coordination sphere, which is an essential requirement for the reaction to proceed, may either be supported by the ancillary ligand through the elongation of the Zr–N_{amine} bonds [7], or by increasing the coordination number of the metal centre. Complexes incorporating this ancillary ligand have shown to be able to accommodate coordination numbers up to 8, which have been characterized by either X-ray diffraction studies or DFT calculations [15]. Overall, the two mechanistic pathways are valid and the presently available information does not allow us to distinguish between them.

In conclusion, a new class of zirconium compounds supported by a cyclam-based ligand was found to competently catalyze the intramolecular hydroamination of selected primary aminoalkenes. To the best of our knowledge this is the first example where a metal macrocyclic complex is used to promote this transformation. The system shows some remarkable features that make it appealing. The fact the ancillary ligand Zr–N bonds resist protonation, which may be related to the macrocyclic effect, is encouraging if one considers the lack of steric hindrance around the amido donors. The absence of free ligand in solution points toward the robust nature of the ligand framework, which is a crucial aspect considering that under catalytic conditions sequential transamination reactions are required for successive catalytic turnovers. We are currently pursuing this study to clarify mechanistic aspects and optimize the system performance, and we are also interested in broadening the substrate scope in hydroamination reactions.

3. Experimental section

3.1. General procedures

All manipulations were performed under a dry nitrogen atmosphere using standard Schlenk and glove box techniques. Solvents were previously dried with 4 Å molecular sieves and distilled under a dry nitrogen atmosphere over sodium/benzophenone (diethyl ether and toluene). Toluene-d_8 and benzene-d_6 were dried with 4 Å molecular sieves, degassed and stored under nitrogen. Literature methods were used to prepare H_2(Bn_2Cyclam), (Bn_2Cyclam)$ZrCl_2$, (Bn_2Cyclam)Zr(CH_2Ph)$_2$, and (($C_6H_4CH_2$)$_2$Cyclam)Zr [8,9].

NMR spectra were recorded on Bruker Avance^{II} 300 MHz or Bruker Avance^{II} 400 MHz spectrometers. Chemical shifts for ^{1}H were referenced to resonances of the residual protonated solvents relative to tetramethylsilane (0 ppm), and ^{13}C spectra were referenced to the solvent carbon resonance. Elemental analysis and low resolution electron ionization were performed at the facilities of the Chemistry Department of the University of British Columbia.

3.1.1. (Bn_2Cyclam)Zr(NMe_2)$_2$ (**1**)

H_2(Bn_2Cyclam) (0.43 g, 1.1 mmol) was dissolved in 10 mL of toluene and slowly added to a −10 °C toluene solution of Zr(NMe_2)$_4$. The resulting pale yellow solution was left stirring overnight. The solvent was evaporated and the residue washed with minimal hexanes to yield (Bn_2Cyclam)Zr(NMe_2)$_2$ in 82% (0.53 g). ^{1}H NMR (C_6D_6, 400.2 MHz): δ(ppm) 7.15–7.10 (overlapping, 6H total, *H*-Ph), 7.05–6.98 (overlapping, 4H total, *H*-Ph), 4.20 (d, 2H, PhCH_2N), 4.02 (d, 2H, PhCH_2N), 3.42 (s, 12H, Zr(N(CH_3)$_2$)$_2$), 3.40–3.23 (overlapping, 6H total, 4H, [C2]CH_2N, 2H, [C3]CH_2N), 3.14 (m, 2H, [C3]CH_2N), 2.86 (m, 2H, [C2]CH_2N), 2.71 (m, 2H, [C3]CH_2N), 2.36 (m, 2H, [C2]CH_2N), 2.18–1.98 (overlapping, 4H total, 2H, 2H, [C3]CH_2N, 2H, $CH_2CH_2CH_2$), 1.64 (m, 2H, $CH_2CH_2CH_2$). ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz): 133.5 (*i*-Ph), 132.1 (*o*-Ph), 128.1 (*m*-Ph), 127.8 (*p*-Ph), 58.8 (PhCH_2N), 56.9 ([C2]CH_2N), 54.6 ([C3]CH_2N), 54.2 ([C2]CH_2N), 48.2 (Zr(N(CH_3)$_2$)$_2$), 46.1 ([C3]CH_2N), 24.6 ($CH_2CH_2CH_2$). Anal. Calcd. for $C_{28}H_{46}N_6Zr$: C 60.28, H 8.31, N 15.06. Found: C 60.11, H 8.01, N 15.03.

3.1.2. (Bn_2Cyclam)Zr(NH$^{2,6\text{-}Me}$Ph)Cl (**2**)

To a THF suspension of (Bn_2Cyclam)$ZrCl_2$ (0.40 g, 0.7 mmol) at −30 °C was slowly added a THF solution of LiNH$^{2,6\text{-}Me}$Ph (0.09 g in 20 mL). During the addition process the suspension starts to dissolve and a pale yellow solution is formed. The mixture was left stirring overnight and the solvent was evaporated. The residue was extracted with toluene, allowing the removal of LiCl. The solvent was evaporated and 10 mL of hexanes were added to wash the yellow residue. A pale yellow solid was obtained in 74% yield (0.32 g). ^{1}H NMR (toluene-d_8, 400.2 MHz, 246 K): δ(ppm) 7.40–7.00 (overlapping, 12H total, 10H, *H*-PhCH$_2$, 2H, *m*-$^{2,6\text{-}Me}$Ph), 6.86 (t, 1H, *p*-$^{2,6\text{-}Me}$Ph), 5.68 (s, 1H, $^{2,6\text{-}Me}$Ph(*H*)NZr), 4.93 (d, $^2J_{HH}$ = 14 Hz, 1H, PhCH_2N), 4.64–4.45 (overlapping, 2H total, 1H, PhCH_2N, 1H, [C3]CH_2N), 4.39 (d, $^2J_{HH}$ = 14 Hz, 1H, PhCH_2N), 4.19–4.04 (overlapping, 2H total, 1H, PhCH_2N, 1H, [C3]CH_2N), 3.61–3.41 (overlapping, 3H total, 2H [C2]CH_2N, 1H, [C3]CH_2N), 2.88 (s, 3H, CH_3-Ph), 2.80–2.50 (overlapping, 7H total, 3H, [C3]CH_2N, 4H, [C2]CH_2N), 2.45–2.30 (overlapping, 4H total, 3H, CH_3-Ph, 1H, [C3]CH_2N), 2.27 (m, 1H, [C3]CH_2N), 2.17 (m, 1H, [C2]CH_2N), 1.96 (m, 1H, [C2]CH_2N), 1.57 (m, 2H, $CH_2CH_2CH_2$), 1.24 (m, 1H, $CH_2CH_2CH_2$), 1.06 (m, 1H, $CH_2CH_2CH_2$). ^{13}C{^{1}H} NMR (toluene-d_8, 100.6 MHz, 246 K): δ(ppm) 155.3 (*i*-$^{2,6\text{-}Me}$PhN), 133.5 (*C*-PhCH$_2$N), 133.3 (*C*-PhCH$_2$N), 132.7 (*i*-Ph), 132.1 (*i*-Ph), overlapping with toluene-d_8 (*i*-Ph and *C*-Ph), 118.06 (*p*-$^{2,6\text{-}Me}$Ph), 57.5 (PhCH$_2$N), 56.9 (PhCH$_2$N), 56.7 ([C3]CH$_2$N), 56.1 ([C3]CH$_2$N), 55.8 ([C3]CH$_2$N), 52.7 ([C2]CH$_2$N), 52.4 ([C2]CH$_2$N), 48.8 ([C2]CH$_2$N), 48.6 ([C2]CH$_2$N), 24.2 ($CH_2CH_2CH_2$), 24.1 ($CH_2CH_2CH_2$), 22.2 ((CH_3)$_2$Ph), 22.0 ((CH_3)$_2$Ph). Anal. Calcd. for $C_{32}H_{44}N_5ClZr$: C 61.46, H 7.09, N 11.20. Found: C 61.56, H 7.49, N 11.08.

3.1.3. (Bn_2Cyclam)Zr(N$^{2,6\text{-}Me}$Ph) (**3**)

To a THF solution of (Bn_2Cyclam)Zr(NH$^{2,6\text{-}Me}$Ph)Cl (0.30 g, 0.5 mmol in 10 mL) was slowly added 1 mL of a diethyl ether solution of MgClMe (0.5 M). During the addition process the light yellow solution becomes turbid. The mixture was allowed to stir overnight, after which the solvent was evaporated. A mixture of 10 mL of toluene, 0.5 mL of THF and 10 mL of dioxane was added to separate $MgCl_2$. After 3 h, the suspension was filtered, taken to dryness and washed with hexanes. The product was obtained in 68% yield (0.20 g). ^{1}H NMR (benzene-d_6, 400.1 MHz, 298 K): δ(ppm) 7.55–6.95 (overlapping, 12H total, 10H, *H*-PhCH$_2$, 2H, *m*-$^{2,6\text{-}iPr}$Ph), 6.65 (t, 1H, *p*-$^{2,6\text{-}iPr}$Ph), 4.51 (d, $^2J_{HH}$ = 14 Hz, 2H, PhCH_2N), 4.32 (d, $^2J_{HH}$ = 14 Hz, 2H, PhCH_2N), 3.97 (m, 2H, [C3]CH_2N), 3.59 (m, 2H, [C2]CH_2N), 3.00–2.80 (overlapping, 5H total, 2H, [C3]CH_2N, 3H, (CH_3)Ph), 2.72–2.50 (overlapping, 9H total, 4H, [C2]CH_2N, 2H, [C3]CH_2N, 3H, (CH_3)Ph), 2.24 (m, 2H, [C3]CH_2N), 2.11 (m, 2H, [C2]CH_2N), 1.47 (m, 2H, $CH_2CH_2CH_2$), 1.02 (m, 2H, $CH_2CH_2CH_2$). ^{13}C{^{1}H} NMR

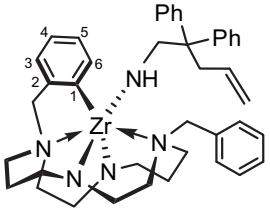
(benzene-d_6, 100.6 MHz, 298 K): δ(ppm) 163.2 (*i*-$^{2,6\text{-Me}}$PhN), 133.0 (*i*-PhCH$_2$N), 131.8 (*C*-Ph), 129.3 (*C*-Ph), 128.6 (*C*-Ph), 128.4 (*C*-Ph), 125.9 (*i*-Ph), 112.7 (*p*-$^{2,6\text{-Me}}$Ph), 56.6 (PhCH$_2$N), 55.8 ([C3]CH$_2$N), 52.3 ([C2]CH$_2$N), 50.1 ([C3]CH$_2$N), 49.9 ([C2]CH$_2$N), 24.8 (CH$_2$CH$_2$CH$_2$), 21.4 ((CH$_3$)$_2$Ph). EIMS (*m*/*z*): 587 (M$^+$). Anal. Calcd. for $C_{32}H_{43}N_5Zr$: C 65.26, H 7.36, N 11.89. Found: C 62.73, H 7.28, N 10.34.

3.1.4. (Bn$_2$Cyclam)Zr(NHCH$_2$CPh$_2$CH$_2$CH=CH$_2$)$_2$ (**6**)

At room temperature, addition of two equivalents of 1-amino-2,2-diphenyl-4-pentene to a C_6D_6 solution of **4** (20 mg, 0.021 mmol) led to quantitative formation of the bis(amido) zirconium complex **6** and toluene as shown by ^{1}H and ^{13}C NMR spectra.

Complex **6** was also obtained by reaction of compounds **1** and **5** with two equivalents of 1-amino-2,2-diphenyl-4-pentene in the same experimental conditions. Formation of $HNMe_2$ was observed in the reaction with **1** as confirmed by a doublet at 2.20 ppm in the ^{1}H NMR spectrum and a resonance at 39.3 ppm in the ^{13}C spectrum that account for the methyl groups of the secondary amine.

^{1}H NMR (C_6D_6, 500.1 MHz, 296 K): δ(ppm) 7.44 (m, 4H, *o*-Ph$_2$C), 7.21–7.13 (overlapping, 12H total, 4H, *o*-PhCH$_2$N, 4H, *m*-PhCH$_2$N, 4H, *m*-Ph$_2$C), 7.09 (m, 2H, *p*-PhCH$_2$N or *p*-Ph$_2$C), 7.03 (m, 2H, *p*-PhCH$_2$N or *p*-Ph$_2$C), 5.85 (m, 2H, −CH=), 5.24 (dd, 2H, =CH$_2$), 5.02 (dd, 2H, =CH$_2$), 4.54 (m, 4H, −NH−CH$_2$), 3.94 (AB system, 4H, PhCH$_2$N), 3.63 (t, 2H, [C3]NCH$_2$), 3.38 (t, 2H, −NH), 3.33 (m, 2H, −CH$_2$−CH=), 3.24 (m, 2H, [C2]NCH$_2$), 3.12 (m, 2H, −CH$_2$−CH=), 3.03–2.99 (overlapping, 4H total, 2H, [C3]NCH$_2$, 2H, [C2]NCH$_2$), 2.54–2.51 (overlapping, 4H total, 2H, [C2]NCH$_2$, 2H, [C2]NCH$_2$), 2.47 (m, 2H, [C3]NCH$_2$), 2.19 (t, 2H, [C3]NCH$_2$), 1.67 (m, 2H, CH$_2$CH$_2$CH$_2$), 1.57 (m, 2H, CH$_2$CH$_2$CH$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 296 K): δ (ppm) 149.0 (*i*-Ph$_2$C), 148.9 (*i*-Ph$_2$C), 136.7 (−CH=), 133.2 (*i*-PhCH$_2$N), 133.0 (*p*-PhCH$_2$N or *p*-Ph$_2$C), 129.7 (*o*-Ph$_2$C), 129.5, 126.2 (*o*-PhCH$_2$N, *m*-PhCH$_2$N, *m*-Ph$_2$C), 126.0 (*p*-PhCH$_2$N or *p*-Ph$_2$C), 117.5 (=CH$_2$), 58.5 (PhCH$_2$N and −NH−CH$_2$), 56.8 ([C3]NCH$_2$), 53.8 (Ph$_2$C), 53.6 ([C2]NCH$_2$ and [C2]NCH$_2$), 51.9 ([C3]NCH$_2$), 43.0 (−CH$_2$−CH=), 25.5 (CH$_2$CH$_2$CH$_2$).



3.1.5. ((C$_6$H$_4$CH$_2$)BnCyclam)Zr(NHCH$_2$CPh$_2$CH$_2$CH=CH$_2$) (**7**)

At room temperature, addition of one equivalent of 1-amino-2,2-diphenyl-4-pentene to a C_6D_6 solution of **5** (23 mg, 0.049 mmol) resulted in the immediate formation of a yellow solution. ^{1}H and ^{13}C NMR analysis revealed formation of the mono-orthometalated complex **7** in a quantitative yield. Full assignment of the aromatic resonances was not possible due to the complexity of the ^{1}H and ^{13}C spectra. ^{1}H NMR (C_6D_6, 400.1 MHz, 296 K): δ(ppm) 8.29 (d, 1H, *H(6)*-Ph), 7.42 (t, 1H, *H(5)*-Ph), 7.34–6.95 (overlapping, 17H total, 1H, *H(4)*-Ph, 1H, *H(3)*-Ph, 2H, *o*-PhCH$_2$N, 2H, *m*-PhCH$_2$N, 1H, *p*-PhCH$_2$N, 4H, *o*-Ph$_2$C, 4H, *m*-Ph$_2$C, 2H, *p*-Ph$_2$C), 5.67 (m, 1H, −CH=), 5.02 (dd, 1H, =CH$_2$), 4.88 (dd, 1H, =CH$_2$), 4.76 (d, 1H, $^2J_{HH}$ = 13 Hz, PhCH$_2$N), 4.31 (m, 2H, −NH−CH$_2$), 4.10 (d, 1H, $^2J_{HH}$ = 14 Hz, PhCH$_2$N), 3.82 (t, 1H, [C3]NCH$_2$), 3.60 (m, 1H, [C2]NCH$_2$), 3.52 (d, 1H, $^2J_{HH}$ = 14 Hz, PhCH$_2$N), 3.40–3.32 (overlapping, 3H total, 1H, −NH, 1H, [C3]NCH$_2$, 1H, [C2]NCH$_2$), 3.20 (m, 1H, −CH$_2$−CH=), 3.04–2.96 (overlapping, 2H total, 1H, −CH$_2$−CH=, 1H, [C2]NCH$_2$), 2.86 (m, 1H, [C3]NCH$_2$), 2.84 (d, 1H, $^2J_{HH}$ = 13 Hz, PhCH$_2$N), 2.77–2.67 (overlapping, 3H total, 1H, [C2]NCH$_2$, 1H, [C2]NCH$_2$, 1H, [C3]NCH$_2$), 2.62–2.45 (overlapping, 2H total, 1H, [C2]NCH$_2$, 1H, [C3]NCH$_2$), 2.36 (m, 1H, [C3]NCH$_2$), 2.24 (m, 1H, [C3]NCH$_2$), 2.14–2.05 (overlapping, 3H total, 1H, [C2]NCH$_2$, 1H, [C2]NCH$_2$, 1H, [C3]NCH$_2$), 1.61–1.47 (overlapping, 1H, CH$_2$CH$_2$CH$_2$, 1H, CH$_2$CH$_2$CH$_2$), 1.10 (m, 1H, CH$_2$CH$_2$CH$_2$), 0.79 (m, 1H, CH$_2$CH$_2$CH$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 296 K): δ(ppm) 187.8 (*C(1)*-Ph), 149.9 (*C(2)*-Ph), 148.7 (*i*-Ph$_2$C), 148.6 (*i*-Ph$_2$C), 139.1 (*C(6)*-Ph), 135.9 (−CH=), 133.3 (*i*-PhCH$_2$N), 132.7, 129.3, 129.3 (*C(5)*-Ph), 128.2, 128.1, 128.1, 127.9, 126.8, 125.8, 125.5, 124.4, 117.5 (=CH$_2$), 62.7 (PhCH$_2$), 59.3 ([C3]NCH$_2$), 58.3 (−NH−CH$_2$), 57.1 (PhCH$_2$), 55.2 ([C2]NCH$_2$), 54.6 ([C3]NCH$_2$), 54.3 ([C3]NCH$_2$), 53.3 (Ph$_2$C), 52.2 ([C2]NCH$_2$), 52.0 (CH$_2$N), 50.6 (CH$_2$N), 49.1 (CH$_2$N), 42.1 (−CH$_2$−CH=), 24.7 (CH$_2$CH$_2$CH$_2$), 24.5 (CH$_2$CH$_2$CH$_2$).

3.2. General procedures for catalytic hydroamination

All hydroamination reactions were carried out in an N_2-filled glove box on an NMR-tube scale. The NMR-tubes were equipped with a Teflon screw cap. The aminoalkene, the standard (1,3,5-trimethoxybenzene) and the catalysts were dissolved in toluene-d_8. The reactions were heated in an oil bath to 115 °C. The heterocyclic products were characterized by ^{1}H and ^{13}C NMR spectroscopy and compared with literature data.

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