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Intramolecular Hydroamination Reactions Catalyzed by Neutral and Cationic Group IV Pyridylamido Complexes

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Zr^{IV} and Hf^{IV} benzyl (neutral or cationic) and amido catalysts stabilized by pyridylamido ligands are found to be good candidates for the intramolecular hydroamination/cyclization of primary and secondary aminoalkenes. In particular, cationic monobenzyl derivatives have shown remarkable catalytic activity for the production of five and six-membered N-containing heterocycles from secondary amino alkenes. In addition, Zr^{IV} and Hf^{IV} amido derivatives that are produced by a temperature-controlled prototropic rearrangement have provided evidence of the central role played by the metal coordination sphere in promoting such catalytic transformations efficiently.

Introduction

Group IV amidopyridinate complexes are among the most studied and successfully employed post-metallocene catalysts for the efficient upgrading of non-activated olefin substrates.[1] Many of these systems have recently played an essential role in the development of new polyolefin materials[1,2] and in the elucidation of knotty and original organometallic aspects.[1,3,4] Widening the application range of exceptional C–C bond-forming catalyst precursors is a challenging research issue of great interest for both academia and industry. To this aim, metal-mediated and selective C–N bond formation reactions represent a stimulating research area for the production of N-containing compounds of potential application in pharmaceutical and fine chemical syntheses. Although there are many synthetic routes to C–N bonds, the hydroamination reaction,[5] a formal N–H addition to unsaturated C–C bonds, provides a convenient pathway and easy access to a variety of N-containing compounds. In the last two decades, the number of publications on hydroamination reactions has sharply grown and early studies on alkali[6] and rare-earth[7] metal catalysts have set the way to the development of highly efficient and selective *d*-block transition metal complexes.[8–12] Recent achievements in the field have stressed the importance of rethinking molecular frameworks in group IV metal catalysts to obtain active and selective systems for the intramolecular hydroamination reaction starting from either primary or secondary aminoalkenes. Similar to the story of polymerization catalysts, there have been rapid developments to the group IV metallocenes to make them easily tunable, highly active and selective catalysts from the constraint geometry (CGCs), half-sandwich, and cyclopentadienyl-free series. This choice also satisfies fundamental thermodynamic requirements for the catalytic hydroamination of primary aminoalkenes.[10,11]

Our interest in the hydroamination reaction stems from previous studies on cationic monobenzyl pyridylamido cyclometalated M^{IV}-complexes (M = Zr, Hf) of general formula $[N_2^{Ph}M(CH_2Ph)]^+[B(C_6F_5)_4]^-$ (**2**, Scheme 1 a), which readily engage in highly efficient α-olefin polymerization (C–C bond formation).[4b] In accordance with this, we became intrigued in addressing whether such coordinatively unsaturated cationic species **2** (as well as their neutral dibenzyl precursors, **1**, Scheme 1 a) could also promote intramolecular hydroamination efficiently (C–N bond formation) in the presence of either primary or secondary aminoalkenes.

Recently, some of us highlighted the unusual organometallic behavior of related group IV amido species (Scheme 1 b **3** and **3′**),[4] in which a temperature-controlled σ-bond metathesis/protonolysis took place reversibly over a wide temperature range (238–373 K). The metal coordination sphere was found to change dramatically: from five-coordinated trisamido species stabilized by bidentate monoanionic {N^-,N} ligands (**3**) to six-coordinated bis(amido)mono(amino) complexes featured by tridentate dianionic {N^-,N,C^-} systems (**3′**).[4a] Unlike amido precursors, tailored neutral (**1**) and cationic (**2**) M^{IV}-amidopyridinate benzyl complexes were prepared from $M(Bn)_4$ (Zr^{IV}, Hf^{IV}) as a metal source (Scheme 1 a, **1** and **2**).

In this paper, we report on the catalytic performance of selected complexes from both series in the hydroamination reaction of either primary or secondary aminoalkene substrates. In addition, the present study has also contributed to elucidate

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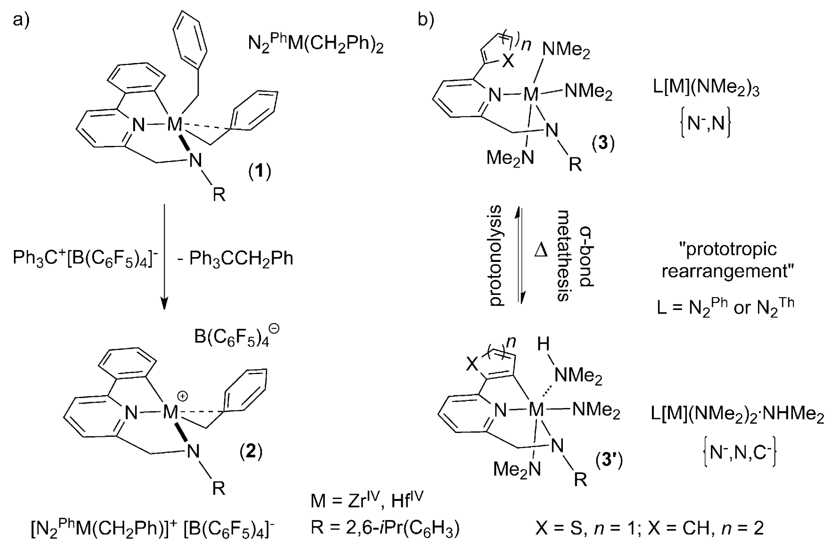


Scheme 1. a) Dibenzyl (**1**) and cationic monobenzyl (**2**) pyridylamido cyclometalated M^{IV}-complexes (M = Zr^{IV}, Hf^{IV}). b) Prototropic rearrangement of group IV amido complexes stabilized by nitrogen-containing ligands capable to undergo reversible and temperature-controlled σ-bond metathesis/protonolysis.

the central role of the metal coordination environment (N^-, N vs. N^-, N, C^- ligated species) on the final catalyst performance.

Results and Discussion

We have recently developed bidentate/tridentate pyridylamido ligands, of the type shown in Scheme 1, bearing aryl or heteroaryl pendant arms as olefin polymerization catalysts in combination with early and rare-earth metals.[1,4,13] Ligand treatment under relatively mild conditions ($T = 70\,^{\circ}C$, $t = 12$–48 h) with $M(Bn)_4$ (M = Zr, Hf; Bn = $CH_2C_6H_5$) as the metal precursor resulted in the formation of M^{IV}-dibenzyl cyclometalated compounds as unique species (**1**, Scheme 1 a).[4b] The reaction did not show any evidence for the generation of intermediates, owing to ability of the ligand to rapidly and quantitatively undergo intramolecular *ortho*-metalation. Complexes $\mathbf{1}_{Zr}$ and $\mathbf{1}_{Hf}$ were prepared in 95% and 93% isolated yields, respectively.[4b] XRD analysis performed on both isolated species unambiguously showed dianionic tridentate {N^-,N,C^-} ligating systems. Whereas crystals of $\mathbf{1}_{Zr}$ for X-ray analysis were straightforwardly obtained by standing a concentrated toluene solution of the complex at room temperature,[4b] suitable X-ray crystals of $\mathbf{1}_{Hf}$ were grown by cooling at $-35\,^{\circ}C$ in a concentrated toluene solution of the complex and layering this with cold drops of *n*-hexane. After maintaining the system at $-35\,^{\circ}C$ for several days, yellow pale microcrystals of $\mathbf{1}_{Hf}$ were separated off. Oak ridge thermal ellipsoid plot (ORTEP) representation of the crystal structure of $\mathbf{1}_{Hf}$ is now given in Figure 1. All the main crystal and structural refinement data are summarized in Table 1, whereas selected bond lengths and angles are summarized in Table S1 (Supporting Information).

$\mathbf{1}_{Hf}$ crystallizes in the triclinic *P*−*1* space group and the asymmetric unit contains one toluene molecule; no special feature is to be underlined, and the main structural parameters (Table S1) are very similar to those obtained for the previously reported Zr^{IV} analogue.[4b] The ligand coordination mode and its κ^3-{N^-,N,C^-} hapticity are also of the same kind. As seen for the Zr^{IV} complex, one of the two benzyl groups in the crystal is η^2-bound to the metal ion [*d*(Hf–C(25)) = 2.233(3) Å; *d*(Hf–C(26)) = 2.771(3) Å; α(Hf–C(25)–C(26)) = 94.18(2)°, whereas the other has η^1-coordination *d*(Hf–C(32)) = 2.235(3) Å; *d*(Hf–C(33)) = 3.161(2) Å; α(Hf–C(32)–C(33)) = 114.75(2)°].

π–π Interactions between the η^2-bound benzyl group and the pyridine ligand are present: the distance between the C_6H_5 group centroid and the plane of the pyridine ring is 3.485 Å, and an angle of 22.0(2)° is formed between the benzyl and pyridine planes. Cationic monobenzyl derivatives $\mathbf{2}_{Zr}$ and $\mathbf{2}_{Hf}$ were prepared in situ upon treatment of $\mathbf{1}_{Zr}$ and $\mathbf{1}_{Hf}$ with an equimolar amount of $[Ph_3C][B(C_6F_5)_4]$.[4b] Although these have limited solubility in aromatic hydrocarbons such as benzene or toluene at room temperature,[4b] $\mathbf{2}_{Zr}$ and $\mathbf{2}_{Hf}$ gave stable dark-green solutions at higher temperatures (solvent boiling points). Before investigating these systems (neutral and cationic species) in catalytic hydroamination reactions, the stability of the cyclometalated forms in the presence of model primary aminoalkenes were properly addressed. Indeed, permanent catalyst modifications in the presence of plain α-olefins, resulting from alkene insertion into the reactive C_{Ar}–M bond, have been extensively claimed by the scientific community as factors that add layers

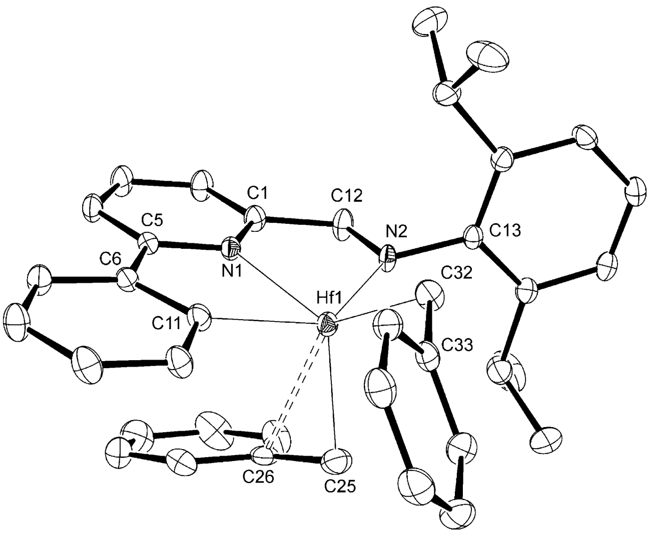
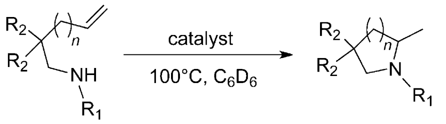


Figure 1. Crystal structure of $N_2^{Ph}Hf(CH_2Ph)_2$ ($\mathbf{1}_{Hf}$). Thermal ellipsoids are drawn at the 40% probability level. Hydrogen atoms and one toluene molecule as the crystallization solvent are omitted for clarity.

Table 1. Crystal data and structure refinement for complexes $\mathbf{1}_{Hf}$, $\mathbf{3}_{Ph,Zr}$, $\mathbf{4}_{Th,Zr}$ and $\mathbf{4}_{Th,Hf}$.

		$\mathbf{1}_{Hf}\cdot C_7H_8$	$\mathbf{1}_{Zr}$[a]	$\mathbf{3}_{Ph,Zr}$	$\mathbf{4}_{Th,Zr}$	$\mathbf{4}_{Th,Hf}$
CCDC number		882101	829625	882103	882102	882104
empirical formula		$C_{38}H_{40}HfN_2\cdot C_7H_8$	$C_{38}H_{40}N_2Zr$	$C_{30}H_{45}N_5Zr$	$C_{26}H_{36}N_4SZr$	$C_{26}H_{36}HfN_4S$
formula weight	[g mol^{-1}]	795.34	614.22	566.93	527.87	615.14
T	[K]	120 (2)	100 (2)	120 (2)	120 (2)	120 (2)
wavelength	[Å]	0.71069	0.71069	0.71069	0.71069	0.71069
crystal system, space group		triclinic, $P\ -1$	monoclinic, $P\ 2_1/n$	orthorhombic, $Pbca$	monoclinic, $P\ 2_1/n$	monoclinic, $P\ 2_1/n$
a	[Å]	9.841(3)	9.522(7)	21.994(2)	19.016(5)	10.687(5)
b	[Å]	9.888(3)	21.178(14)	15.315(1)	14.169(5)	18.284(9)
c	[Å]	19.767(6)	16.076(17)	35.931(3)	19.964(5)	13.563(6)
α	[°]	87.794(2)	90	90	90	90
β	[°]	89.871(2)	106.769(10)	90	91.854	96.169(4)
γ	[°]	74.050(2)	90	90	90	90
V	[Å^3]	1848.0(9)	3104(4)	12 103(2)	5376(3)	2634.9(2)
Z, D_c	[g m^{-3}]	2, 1.429	4, 1.318	16, 1.245	8, 1.304	4, 1.551
absorption coefficient	[mm^{-1}]	2.856	0.383	0.389	0.506	4.058
$F(000)$		808	1288	4800	2208	1232
crystal size	[mm]	0.05×0.05×0.1	0.01×0.05×0.05	0.01×0.01×0.01	0.04×0.05×0.05	0.01×0.013×0.02
θ range for data collection	[°]	4.24:32.87	3.85:26.46	4.10:26.99	4.09:29.15	4.12:29.37
limiting indices		$-14\leq h\leq 14$	$-11\leq h\leq 10$	$-24\leq h\leq 26$	$-25\leq h\leq 25$	$-14\leq h\leq 14$
		$-14\leq k\leq 14$	$-22\leq k\leq 26$	$-18\leq k\leq 17$	$-18\leq k\leq 18$	$-24\leq k\leq 24$
		$-30\leq l\leq 28$	$-18\leq l\leq 15$	$-44\leq l\leq 40$	$-25\leq l\leq 26$	$-18\leq l\leq 17$
reflections collected/unique		29 941/12 333	14 873/4629	89 972/11 350	57 569/12 789	33 738/6402
GOF on F^2		1.059	0.979	0.943	1.032	1.078
data/restraints/parameters		12 333/0/438	4629/0/370	11 350/0/663	12 789/0/617	6402/0/297
final R indices	[$I>2\sigma(I)$]	$R1=0.0331$	$R1=0.0382$	$R1=0.0851$	$R1=0.0540$	$R1=0.0409$
		$wR2=0.0724$	$wR2=0.0822$	$wR2=0.1599$	$wR2=0.0986$	$wR2=0.0888$
R indices (all data)	[$I>2\sigma(I)$]	$R1=0.0390$	$R1=0.0626$	$R1=0.2551$	$R1=0.1119$	$R1=0.0589$
		$wR2=0.0762$	$wR2=0.0884$	$wR2=0.2232$	$wR2=0.1216$	$wR2=0.1021$
largest diffraction peak/hole	[e Å^{-3}]	1.956/−1.497	0.391/−0.392	2.146/−0.707	0.636/−0.721	2.998/−1.652

[a] Selected data from Ref. [4b], listed here for completeness.



4	n=1	R_2 = Ph	R_1 = H
5	n=1	R_2 = CH_3	R_1 = H
6	n=1	R_2 = Ph	R_1 = Me
7	n=1	R_2 = -$(CH_2)_5$-	R_1 = H
8	n=2	R_2 = CH_3	R_1 = Me

Scheme 2. Intramolecular hydroamination of primary and secondary amines.

of complexity to the identification of the active species operating in polymerization catalysis.[3,4b,14] Unlike plain olefinic systems, aminoalkenes **4** and **5** (Scheme 2) did not show any ligand/complex modification on both neutral and cationic forms (**1** and **2**), even after prolonged heating in toluene under reflux. Experimental evidence was given by the analysis of the GC–MS traces of the hydrolyzed reaction mixtures resulting from either stoichiometric (complex/substrate = 1:1) or sub-stoichiometric (complex/substrate = 1:3) cyclization tests (see Figure S1 and related experimental details in the Supporting Information). Three main peaks from selected trials [$(m/z-1)_{aminoalkene}=236$, $(m/z=237)_{pyrrolidine}$ and $(m/z=344)_{ligand}$ from $\mathbf{1}_{Zr}$/**4**; $(m/z-1)_{aminoalkene}=112$, $(m/z)_{pyrrolidine}=113$ and $(m/z)_{ligand}=343$ g mol^{-} from $\mathbf{2}_{Hf}$/**5**] were unambiguously attributed to the expected hydroamination products, the residual aminoalkenes and the totally unmodified ligand, respectively. Although a definitive explanation for the different chemical behavior of aminoalkenes from plain olefins has yet to be provided in a straightforward manner (it would also beyond the scope of this work), it seems reasonable that amido/imido cyclization intermediates sterically prevent olefin insertion into the C_{Ar}–M bond. Accordingly, the ability of complexes $\mathbf{1}_{Zr}$ and $\mathbf{1}_{Hf}$ to promote the hydroamination/cyclization of primary and secondary amines tethered to monosubstituted alkenes has been systematically scrutinized (Scheme 2, Table 2).

As shown in Table 2, both neutral complexes are active catalysts for the hydroamination reaction of primary aminoalkenes (Table 2, entries 1–6). Indeed, 10 mol % of $\mathbf{1}_{Zr}$ allows the almost complete (>95 %) and total regioselective cyclization of the *gem*-diphenyl aminopentene **4** after 2 h at 100 °C (entry 1). Slightly longer reaction times is required to complete the cyclization of the less Thorpe–Ingold-activated substrate **7** (entry 3). Similarly to other preceding literature,[10] the activity of the zirconium complex ($\mathbf{1}_{Zr}$) is markedly superior to that measured for the hafnium counterpart ($\mathbf{1}_{Hf}$) with both primary aminoalkenes investigated (entries 4–6); over ten-fold longer reaction times were required to completely convert **4** into the corresponding pyrrolidine derivative while passing from $\mathbf{1}_{Zr}$ to $\mathbf{1}_{Hf}$ (entries 5 vs. entry 1). At odds with primary aminoalkenes, both neutral dibenzyl complexes show rather scarce activities in the presence of substrates containing secondary amine groups. As a matter of fact, the most active $\mathbf{1}_{Zr}$ provides only 45 % conversion of **6** into the desired pyrrolidine derivative

Table 2. Intramolecular hydroamination of primary and secondary aminoalkenes catalyzed by neutral and cationic Zr^{IV} and Hf^{IV} complexes.[a]

Entry	Catalyst	Substrate	t [h]	Conversion[b] [%]
1	$\mathbf{1}_{Zr}$	**4**	2	> 95
2		**6**	20	45[c]
3		**7**	3	> 97
4	$\mathbf{1}_{Hf}$	**4**	2	77
5		**4**	20	92
6		**7**	23	86
7	$\mathbf{2}_{Zr}$	**4**	2	> 97
8		**6**	0.25	> 98
9		**7**	8	93
10		**8**	0.25	> 98
11	$\mathbf{2}_{Hf}$	**4**	2	> 98
12		**6**	0.25	> 98
13		**7**	16	93
14		**8**	0.25	> 98

[a] Reactions were performed in C_6D_6 at 100 °C under argon with 10 mol % of catalyst, unless otherwise stated. [b] Determined by in situ ^1H NMR spectroscopy. [c] In the presence of over 20 mol % of byproducts.

(entry 2) after 20 h reaction time under the same catalytic conditions used for the primary amino substrates **4** and **7**. Additionally, over 20 mol % of byproducts arising from a ß-hydride elimination path are detected by ^1H MNR spectroscopy. Such a competitive side-reaction has been earlier observed in Group IV metal-catalyzed intramolecular hydroamination with secondary aminoalkenes.[10c]

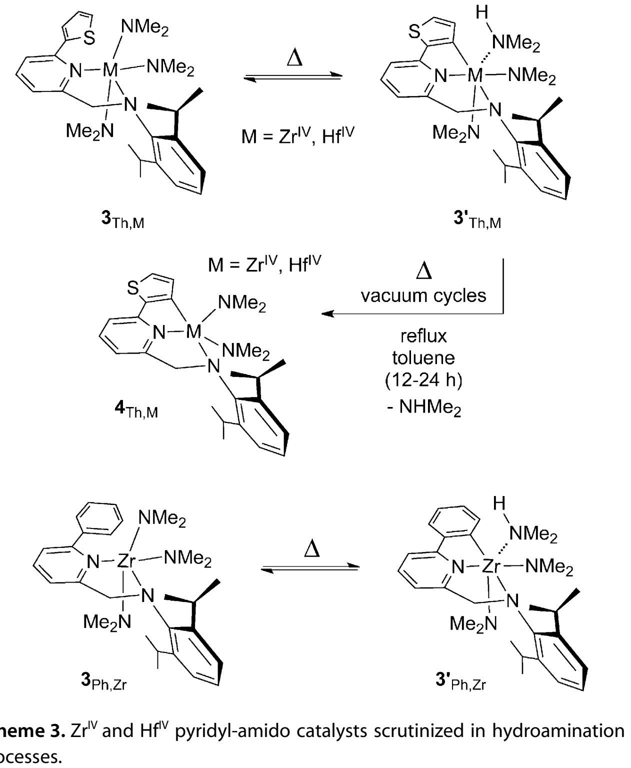
On the other hand, cationic monobenzyl complexes $\mathbf{2}_{Zr}$ and $\mathbf{2}_{Hf}$ (prepared in situ upon treatment of neutral precursors with an equimolar amount of $[Ph_3C][B(C_6F_5)_4]$) are capable of catalyzing the hydroamination of primary and secondary aminoalkenes efficiently (Table 2, entries 7–14). Although both cationic species are scarcely soluble in aromatic hydrocarbons at room temperature, they turn out to be completely soluble at the final reaction temperature (100 °C). Both $\mathbf{2}_{Zr}$ and $\mathbf{2}_{Hf}$ catalysts give a complete conversion of **4** into the corresponding pyrrolidine derivative within 2 h (entries 7 and 11), in line with the catalytic activities measured for the neutral compounds $\mathbf{1}_{Zr}$ and $\mathbf{1}_{Hf}$ (entry 7 vs. entry 1 and entry 11 vs. entry 4). However, the less activated primary aminoalkene **7** undergoes cyclization less efficiently in the presence of cationic promoters (entry 9 vs. entry 3). Overall, neutral and cationic Hf^{IV} derivatives are less efficient in the cyclization of primary aminoalkenes compared with their Zr^{IV} counterparts; they require longer reaction times to drive the reaction to completeness (entry 6 vs. entry 3 and entry 13 vs. entry 9).

Notably, the hydroamination of the secondary aminoalkene **6** with both $\mathbf{2}_{Zr}$ and $\mathbf{2}_{Hf}$ resulted in considerably improved reaction rates. Indeed, an almost complete substrate conversion to the desired product was achieved in less than 20 min (entries 8 and 12). Additionally, the formation of a six-membered ring from the *gem*-dimethyl *N*-methylaminohexene **8** was conveniently and quantitatively achieved in 20 min with both cationic catalysts (entries 10 and 14).[15,16] No traces of hydroaminoalkylation[17] side-products were ever observed during the cyclization of **8**.[18] Overall, both cationic forms $\mathbf{2}_{Zr}$ and $\mathbf{2}_{Hf}$, present remarkable reactivities in the hydroamination reaction, particularly for the cyclization of secondary aminoalkenes. These results are even more interesting if compared with those based on other cationic group IV metal complexes reported in the literature so far (referring to both five-[9] and six-membered[9a] cyclizations).

Only a few systems based on group IV metals are effective catalysts for the hydroamination of both primary and secondary aminoalkenes.[9c,10g,j] As a general trend, cationic group IV metal complexes are restricted to the cyclization of secondary aminoalkenes, whereas they are (with rare exceptions)[9c] almost inactive systems for the cyclization of primary amino substrates.[9a,b] Herein, cationic monobenzyl Zr^{IV} and Hf^{IV} complexes $\mathbf{2}_{Zr}$ and $\mathbf{2}_{Hf}$ have demonstrated their ability at promoting catalytic hydroamination of both primary and secondary amines with enhanced catalytic activity compared with those reported in the literature and based on group IV metal catalysts.[9c]

In addition to neutral dibenzyl and cationic monobenzyl Zr/Hf complexes, amido derivatives of the type shown in Scheme 1 b have also been investigated as hydroamination catalysts. In particular, the ability of these systems to undergo prototropic rearrangement over a wide temperature range (resulting into a relevant change of the metal coordination sphere) was taken into account to elucidate the role of the active site environment on the catalytic performance.

The amido complexes shown in Scheme 3 have already been exploited as polymerization catalysts for the production



Scheme 3. Zr^{IV} and Hf^{IV} pyridyl-amido catalysts scrutinized in hydroamination processes.

of high-density polyethylene (HDPE).[4a] The results of this study have demonstrated that only the *ortho*-metalated forms were responsible for the generation of catalytically active species in polymerization catalysis.

For hydroamination tests, only the thienyl-containing systems ($\mathbf{3}_{Th,Zr}$/$\mathbf{3'}_{Th,Zr}$, and $\mathbf{3}_{Th,Hf}$/$\mathbf{3'}_{Th,Hf}$) were selected, according to their higher ability at undergoing intramolecular σ-bond metathesis and thus providing higher molar fractions of the cyclometalated forms (**3′**) in high temperature solution processes.[19] In addition, the phenyl derivative $\mathbf{3}_{Ph,Zr}$/$\mathbf{3'}_{Ph,Zr}$ (for which the trisamido form was always the most abundant in solution even at high temperatures)[19] was also selected for the sake of comparison. To assess the influence of the metal coordination sphere in catalytic hydroamination tests, unique Hf^{IV} and Zr^{IV}-bisamido derivatives ($\mathbf{4}_{Th}$) were synthesized. According to literature procedures, prolonged heating of the tautomeric mixtures ($\mathbf{3}_{Th,M}$/$\mathbf{3'}_{Th,M}$) in toluene under reflux, combined with static vacuum cycles, allowed for the isolation of the bisamido derivatives $\mathbf{4}_{Th,Zr}$ and $\mathbf{4}_{Th,Hf}$ in 93 % and 95 % yields, respectively. Single crystals suitable for XRD studies were straightforwardly grown from concentrated 1:1 toluene/*n*-hexane mixtures of $\mathbf{4}_{Th,Zr}$ and $\mathbf{4}_{Th,Hf}$.

ORTEP drawings of the crystal structures obtained from $\mathbf{4}_{Th,Zr}$ and $\mathbf{4}_{Th,Hf}$ are given in Figure 2 and 3, respectively, whereas Table 2 lists all the main crystal and structural refinement data.

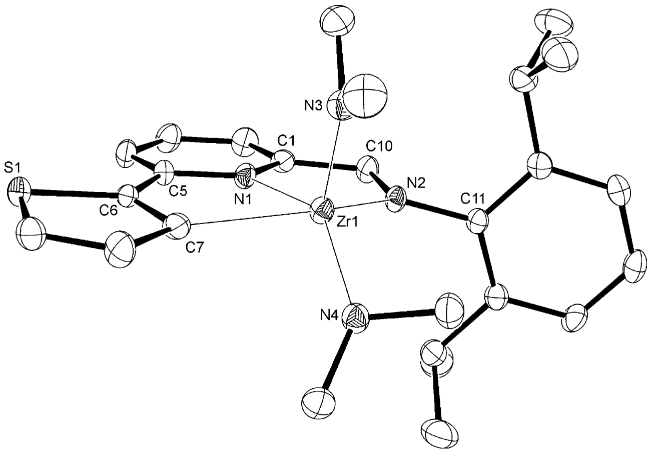


Figure 2. Crystal structure of {N$^-$,N,C$^-$}N$_2^{Th}$Zr(NMe$_2$)$_2$ [$\mathbf{4}_{Th,Zr}$]. Thermal ellipsoids are drawn at the 40 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are summarized in Table S1.

The two compounds are isostructural; they both crystallize in the monoclinic $P2_1/n$ space group. The coordination geometry around the metal centre is similar to that observed in the benzyl analogues.[4b] In the $\mathbf{4}_{Th,Zr}$, two almost identical molecules are present in the asymmetric unit; they are related to each other through a C_2 pseudo-symmetric axis along the *b* direction. Consequently, the same chemical species is "seen" as two structurally different molecules.[20] The unit cell volume and Z in $\mathbf{4}_{Th,Zr}$ are doubled with respect to those of $\mathbf{4}_{Th,Hf}$, and they maintain the same structural features.

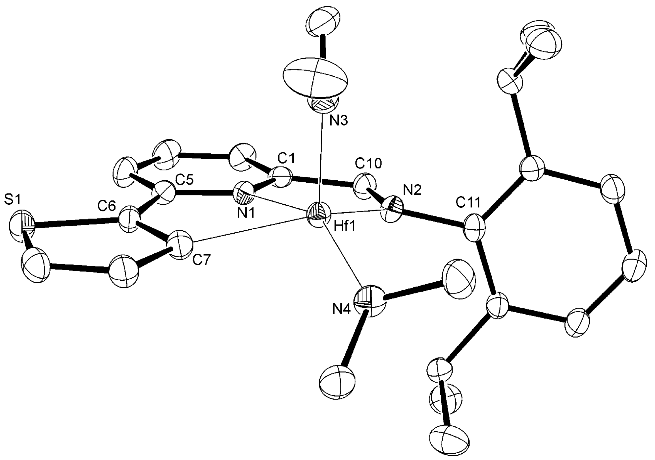


Figure 3. Crystal structure of {N$^-$,N,C$^-$}N$_2^{Th}$Hf(NMe$_2$)$_2$ [$\mathbf{4}_{Th,Hf}$]. Thermal ellipsoids are drawn at the 40 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are summarized in Table S1.

While preparing crystals from cyclometalated forms, we also succeeded in the isolation of crystals of $\mathbf{3}_{Ph,Zr}$. Upon standing for several weeks, yellow pale microcrystals suitable for XRD analysis were separated off from a cooled (−50 °C) and highly diluted toluene solution of $\mathbf{3}_{Ph,Zr}$/$\mathbf{3'}_{Ph,Zr}$.

Previous attempts to isolate single crystals for X-ray analysis from the tautomeric mixture under milder conditions (diluted or concentrated solutions in the −35–0 °C temperature range) failed.[21] An ORTEP drawing of the trisamido-Zr^{IV} species is shown in Figure 4. The compound crystallizes in the orthorhombic *Pbca* space group. The coordination number and geometry of the Zr^{IV} ion are the same as those of the corresponding bisamido analogues; the ligand phenyl ring is dangling, and two molecules with different Py–Ph dihedral angles are present in the asymmetric unit [117.0(11)° and 134.4(9)°, respectively].

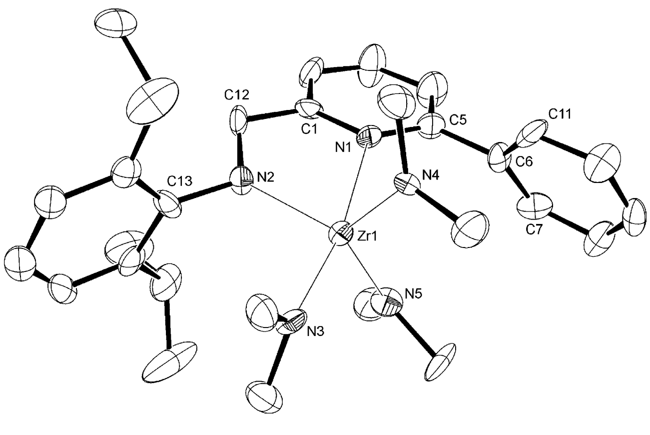


Figure 4. Crystal structure of {N$^-$,N}N$_2^{Ph}$Zr(NMe$_2$)$_3$ [$\mathbf{3}_{Ph,Zr}$]. Thermal ellipsoids are drawn at the 40 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are summarized in Table S1.

The low energy barrier for the phenyl ring rotation around the C(5)–C(6) bond allows for the presence of two different conformers within the same crystal lattice. As a consequence, the unit cell volume (12 103(2) Å^3) and Z value (16) for $\mathbf{3}_{\text{Ph,Zr}}$ are unusually high (four times as much) if compared with those of its cyclometalated benzyl analogue {N$^-$,N,C$^-$}N$_2$$^{\text{Ph}}$Zr(CH$_2$Ph)$_2$.[4b] Refer to Table S1 for the most relevant crystallographic parameters.

All isolated compounds and tautomeric mixtures were used as catalysts for the intramolecular hydroamination of aminoalkene **4** as the model substrate. Unlike the previous catalytic studies performed in a J-Young NMR tube (see experimental section for neutral (alkyl) and cation Zr$^{\text{IV}}$ and Hf$^{\text{IV}}$ complexes), catalytic tests with amido compounds were conducted in a glove box, under an inert atmosphere. The reactions were set-up in a two-necked round bottomed flask equipped with a magnetic stirrer-bar and a septum for the ongoing syringe substrate addition. By this method, the aminoalkene **4** was added to a pre-heated catalyst(s) solution at the final reaction temperature. These conditions were used to achieve a better control of the molar fraction of the cyclometalated species to be put in contact with the substrate; this procedure was of major importance for the catalytic tests performed in the presence of temperature sensitive tautomeric mixtures such as $\mathbf{3}_{\text{Th,M}}$/$\mathbf{3'}_{\text{Th,M}}$ and $\mathbf{3}_{\text{Ph,Zr}}$/$\mathbf{3'}_{\text{Ph,Zr}}$. Catalyst(s) content was fixed to 5 mol % and the reaction temperature (unless otherwise stated) was set at 100 °C. The catalytic assays obtained with different Zr/Hf amido catalysts are shown in Table 3. All complexes showed moderate to high efficiency in the cyclohydroamination reaction of the primary aminoalkene **4**.[22] In particular $\mathbf{4}_{\text{Th,Zr}}$ gave complete substrate conversion to the corresponding pyrrolidine in 1 h (entry 4).

Table 3. Intramolecular hydroamination of **4** (and **6**) by pyridylamido complexes $\mathbf{3}_{\text{Th,M}}$/$\mathbf{3'}_{\text{Th,M}}$, $\mathbf{3}_{\text{Ph,Zr}}$/$\mathbf{3'}_{\text{Ph,Zr}}$ and $\mathbf{4}_{\text{Th,M}}$.[a]

Entry[a]	Catalyst	**3**/**3**′ molar ratio[b]	Substrate	*t* [h]	Conversion[c] (isolated yield)[d] [%]
1	$\mathbf{3}_{\text{Th,Zr}}$/$\mathbf{3'}_{\text{Th,Zr}}$	25:75	**4**	2	92 (87)
2	$\mathbf{3}_{\text{Th,Hf}}$/$\mathbf{3'}_{\text{Th,Hf}}$	11:89	**4**	2	25 (19)[e]
3	$\mathbf{3}_{\text{Ph,Zr}}$/$\mathbf{3'}_{\text{Ph,Zr}}$	62:38	**4**	2	59 (52)
4	$\mathbf{4}_{\text{Th,Zr}}$	–	**4**	1	$>$99 ($>$98)
5	$\mathbf{4}_{\text{Th,Zr}}$	–	**6**	5	n.d.
6	$\mathbf{4}_{\text{Th,Zr}}$[f]	–	**4**	3	94 (90)
7	$\mathbf{4}_{\text{Th,Zr}}$[f]	–	**4**	4	$>$99 ($>$98)
8	$\mathbf{4}_{\text{Th,Zr}}$[g]	–	**4**	3	6 (n.d.)[e]
9	$\mathbf{4}_{\text{Th,Hf}}$	–	**4**	1	19 (16)[e]
10	$\mathbf{4}_{\text{Th,Hf}}$	–	**6**	5	n.d.
11	$\mathbf{4}_{\text{Th,Hf}}$[f]	–	**4**	3	29 (26)[e]
12	$\mathbf{4}_{\text{Th,Hf}}$[f]	–	**4**	72	89 (85)
13	$\mathbf{4}_{\text{Th,Hf}}$[g]	–	**4**	3	$<$1 (n.d.)

[a] Hydroamination conditions: toluene solvent (3 mL), **4** (0.632 mmol, 150 mg), $T = 100$ °C, 5 mol % catalyst. [b] Calculated from the ^{1}H NMR spectrum at the final reaction temperature; see Ref. [4]. [c] Determined by GC–MS. [d] Calculated from the weight of the isolated product after chromatographic purification of the crude mixture. [e] Average values calculated over three independent runs. [f] $T = 80$ °C. [g] RT. Not determined = n.d.

Notably, the comparison of tautomeric catalytic mixtures (**3**/**3**′) with the pure bisamido cyclometalated form (**4**) has contributed to shedding light on important structure-activity relationships for this class of group IV amido-based systems.[4] In particular, pre-catalysts $\mathbf{3}_{\text{Th,Zr}}$/$\mathbf{3'}_{\text{Th,Zr}}$ and $\mathbf{4}_{\text{Th,Zr}}$ had the most active systems under the selected cyclization conditions. Apparently, the metal coordination environment was the most relevant factor for influencing the measured catalytic activities. Unlike **4**, the $\mathbf{3}_{\text{Th,Zr}}$/$\mathbf{3'}_{\text{Th,Zr}}$ mixture was present in 75 % as the bisamido {N$^-$,N,C$^-$} cyclometalated form, at 100 °C (Table 3, entry 1).[4]

Accordingly, the $\mathbf{3}_{\text{Ph,Zr}}$/$\mathbf{3'}_{\text{Ph,Zr}}$ mixture, for which the maximum cyclometalated content (**3**′) at 100 °C was estimated to be 38 %, gave lower substrate conversions (Table 3, entry 3 vs. entry 1). In spite of a higher percentage of the cyclometalated form in the $\mathbf{3}_{\text{Th,Hf}}$/$\mathbf{3'}_{\text{Th,Hf}}$ counterparts (entry 2), worse substrate conversions were (usually) reached if switching from Zr-amido to Hf-amido pre-catalysts (entry 2 vs. entry 1 and entries 4, 6, and 8 vs. entries 9, 11, and 13).[10] According to these data, it is evident that both the metal type (Zr vs. Hf) and their coordination environment play a crucial role in the final catalyst performance. Similarly to our previous studies on polymerization catalysis,[4] cyclometalated group IV pyridylamido systems gave higher substrate conversions. Although a real comparison between unique trisamido {N$^-$,N} and bisamido cyclometalated {N$^-$,N,C$^-$} forms was hampered by the ability of the former to undergo intramolecular cyclometalation (σ-bond metathesis) at high temperature, the observed reactivity trend (**3**/**3**′ mixtures vs. **4** bisamido systems) confirmed the major contribution of the cyclometalated species (**4**). The ability of the latter to perform intramolecular hydroamination was then investigated under different temperature conditions. Whereas $\mathbf{4}_{\text{Th,Zr}}$ gave complete conversion of **4** in 1 h at 100 °C, lowering the temperature to 80 °C resulted in high conversion after 3 h and complete cyclization of **4** after 4 h (entries 4, 6, and 7). The Hf analogue $\mathbf{4}_{\text{Th,Hf}}$ showed only moderate substrate conversions; lowering the reaction temperature to 80 °C required long reaction times to get satisfactory pyrrolidine yields (entries 9, 11, and 12). Preliminary kinetic investigations on complexes $\mathbf{3}_{\text{Th,Zr}}$/$\mathbf{3'}_{\text{Th,Zr}}$ and $\mathbf{4}_{\text{Th,Zr}}$ confirmed the first-order kinetics with respect to the substrate with both catalytic systems (Figure 5).

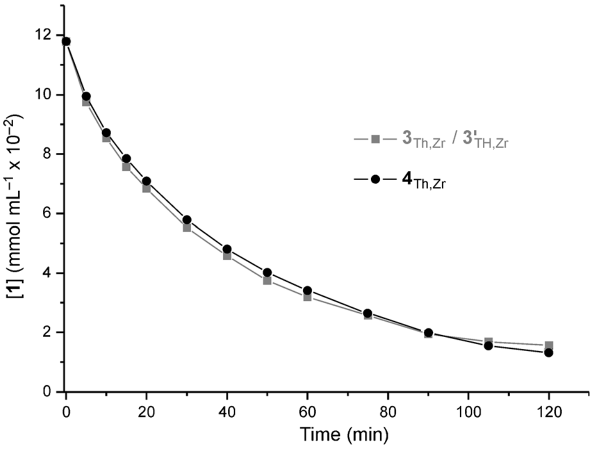


Figure 5. Plot of first-order substrate (**4**) conversion with $\mathbf{3}_{\text{Th,Zr}}$/$\mathbf{3'}_{\text{Th,Zr}}$ and $\mathbf{4}_{\text{Th,Zr}}$ at 5 mol % and 3.75 mol %, respectively.[23]

To get a better comparison of the activity at 100 °C for the two catalytic systems, the kinetic profile resulting from substrate consumption/conversion as obtained from 5 mol% of the $\mathbf{3}_{\mathrm{Th,Zr}}/\mathbf{3'}_{\mathrm{Th,Zr}}$ was compared with that recorded in the presence of 3.75 mol% of $\mathbf{4}_{\mathrm{Th,Zr}}$.[19,23]

As it can be appreciated from Figure 5, there are no significant differences in the catalyst half-lives measured with both catalytic systems [$t_{1/2}$ $\mathbf{3}_{\mathrm{Th,Zr}}/\mathbf{3'}_{\mathrm{Th,Zr}}=28$ min; $t_{1/2}$ $\mathbf{4}_{\mathrm{Th,Zr}}=30$ min]. In addition, the hydroamination reaction performed with the pure $\mathbf{4}_{\mathrm{Th,Zr}}$ catalyst was determined to be first-order in catalyst concentration. The first-order kinetics in catalyst and substrate concentration was previously reported for other neutral zirconium catalysts.[10,24]

Normalized Ln[substrate] versus time plots measured for three different catalyst [$\mathbf{4}_{\mathrm{Th,Zr}}$] concentrations are shown in Figure 6; the inset demonstrates the linearity of the observed *k* values versus catalyst concentration. All these data taken together lead to the conclusion that the two catalytic systems ($\mathbf{3}_{\mathrm{Th,Zr}}/\mathbf{3'}_{\mathrm{Th,Zr}}$ and $\mathbf{4}_{\mathrm{Th,Zr}}$) share a common catalytically active species. Even if a catalytic role of the trisamido species $\mathbf{3}_{\mathrm{Th,Zr}}$ in the $\mathbf{3}_{\mathrm{Th,Zr}}/\mathbf{3'}_{\mathrm{Th,Zr}}$ mixture cannot be fully discarded,[23] it is apparent that its contribution is kinetically negligible under the cyclization conditions applied in these trials. Hydroamination of secondary aminoalkenes with bisamido **4** systems did not take place even after prolonged heating times (Table 3, entries 5 and 10), which is in agreement with most previous studies on neutral group IV metal complexes in the hydroamination reaction.[10,25] This observation supports the hypothesis of imido species as intermediates in the catalytic cycle.[5,10]

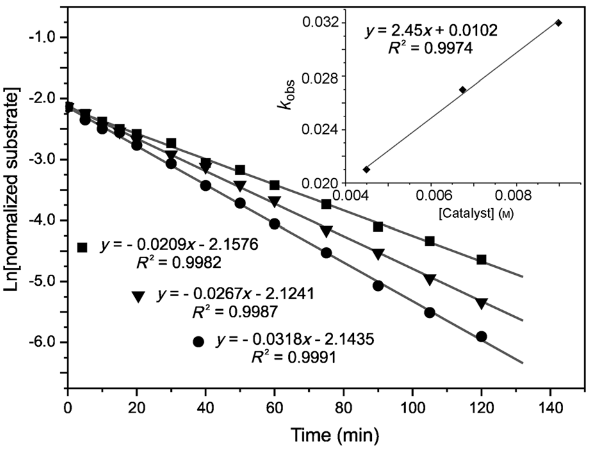


Figure 6. Plot of first-order catalyst dependence for intramolecular hydroamination of **4** at 4 (■), 6 (▼), and 8 mol% (●) concentrations of $\mathbf{4}_{\mathrm{Th,Zr}}$. Inset shows the linearity of the observed *k* values versus catalyst concentration (see also the Supporting Information).

Conclusions

A number of $\mathrm{Zr^{IV}}$ and $\mathrm{Hf^{IV}}$ benzyl and amido state-of-the-art polymerization catalysts are found to be good candidates (in either neutral or cationic form) for the intramolecular hydroamination/cyclization of either primary or secondary aminoalkenes. In particular, cationic monobenzyl derivatives prepared upon treatment of their neutral counterpart with $[\mathrm{Ph_3C}][\mathrm{B(C_6F_5)_4}]$ have shown remarkable catalytic activity for the production of five- and six-membered N-containing heterocycles starting from secondary amino alkenes. In addition, $\mathrm{Zr^{IV}}$ and $\mathrm{Hf^{IV}}$ amido derivatives featured by a temperature-controlled prototropic rearrangement capable of a deep "redrawing" of the metal coordination sphere have been investigated with the specific aim of elucidating the role of the active site environment on the final catalytic performance. To fulfill the latter aspect, unique $\mathrm{Zr^{IV}}$ and $\mathrm{Hf^{IV}}$ bisamido cyclometalated species have been isolated and completely characterized. Their catalytic behavior in the hydroamination reaction combined with preliminary kinetic investigations, have provided evidence of the central role played by the metal coordination sphere in promoting such catalytic transformations efficiently. Overall, this study demonstrates the applicability of pyridylamido group IV metal complexes to the intramolecular hydroamination reaction, which widens the scope of this exceptional class of polymerization catalyst. These findings pave the way to the development of original early-transition metal complexes based on C_1 symmetric N-containing ligands for a stereoselective hydroamination catalysis. Preliminary stereoselective processes are currently ongoing in our laboratories and will be reported soon.

Experimental Section

All air- and/or moisture-sensitive reactions were performed under an inert atmosphere in flame-dried flasks by standard Schlenk-type techniques or in a dry box filled with nitrogen or argon. Benzene and toluene were purified by distillation from sodium/triglyme benzophenone ketyl and stored over activated 4 Å molecular sieves or were obtained by means of an MBraun Solvent Purification System. $[\mathrm{D_6}]$Benzene and $[\mathrm{D_8}]$toluene were dried over sodium/benzophenone ketyl and condensed in vacuo over activated 4 Å molecular sieves prior to use. All other reagents and solvents were used (unless otherwise stated) as purchased from commercial suppliers without further purification. The aminopyridinate ligands **4a** and **4b** were synthesized according to standard procedures reported in the literature.[13] Literature methods were used to synthesize the corresponding $\mathrm{Zr^{IV}}/\mathrm{Hf^{IV}}$-benzyl (neutral, **1** and cationic, **2**) and/or amido complexes **3**/**3′** and **4**.[4] 1D (^{1}H and ^{13}C{^{1}H}) and 2D (COSY H,H, HETCOR H,C) NMR spectra of all organometallic species were obtained on either a Bruker Avance DRX-400 spectrometer (400.13 and 100.61 MHz for ^{1}H and ^{13}C, respectively) or a Bruker Avance 300 MHz instrument (300.13 and 75.47 MHz for ^{1}H and ^{13}C, respectively). Chemical shifts are reported in ppm relative to TMS, referenced to the chemical shifts of residual solvent resonances (^{1}H and ^{13}C). The multiplicities of the ^{13}C{^{1}H} NMR spectra were determined on the basis of the ^{13}C{^{1}H} JMOD sequence and quoted as: $\mathrm{CH_3}$, $\mathrm{CH_2}$, CH and C for primary, secondary, tertiary and quaternary carbon atoms, respectively. Deuterated solvents for NMR measurements were dried over molecular sieves. The C, H, N, S elemental analyses were made at ICCOM-CNR by using a Thermo FlashEA 1112 Series CHNS-O elemental analyzer with an accepted tolerance of ±0.4 units on carbon (C), hydrogen (H) and nitrogen (N).

X-ray data measurements

Single crystal X-Ray data were collected at low temperature (120 K) on an Oxford Diffraction XCALIBUR 3 diffractometer equipped with a CCD area detector by using MoK_{α} radiation ($\lambda = 0.7107$ Å). The program used for the data collection was CrysAlis CCD 1.171.[26] Data reduction was performed with the program CrysAlis RED 1.171[27] and the absorption correction was applied with the program ABSPACK 1.17. Direct methods implemented in Sir97[28] were used to solve the structures and the refinements were performed by full-matrix least-squares against F^2 implemented in SHELX97.[29] All the non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were fixed in calculated positions and refined isotropically with the thermal factor depending on the atoms to which they are bound (riding model). In the refinement of $\mathbf{3}_{Ph,Zr}$, restraints on some anisotropic displacement parameters of C atoms had to be introduced, owing to the bad crystal data quality ($R_{int} = 0.30$) generated by the existence of different conformers in the same lattice (see the Results and Discussion section) and by the disorder of the dimethylamido ligands even at 120 K. Molecular plots were produced by the program ORTEP3.[30] Catalytic reactions were performed under an inert atmosphere in either a J-Young NMR tube or in a 10 mL round bottom flask and the reaction course was followed by ^{1}H NMR spectroscopy and GC–MS analysis, respectively. All substrates were dried overnight over activated 4 Å molecular sieves with a few drops of [D$_6$]benzene prior to use.

General procedure for intramolecular hydroamination of aminoalkenes

Two different cyclization conditions were used depending on the employed catalytic system. Both procedures were set-up under an inert atmosphere with N_2 or an Ar-filled dry box.

Procedure A: Neutral (alkyl) and cationic group IV amidopyridinate complexes were tested as catalyst precursors in the intramolecular hydroamination reaction with a sealed J-Young NMR tube.

For neutral complexes $\mathbf{1}_{Zr}$ and $\mathbf{1}_{Hf}$: In an Ar-filled dry box, a solution of isolated $\mathbf{1}_{Zr}$ or $\mathbf{1}_{Hf}$ (0.016 mmol) in C_6D_6 (0.6 mL) was slowly added to a vial containing the corresponding aminoalkene ($0.16.10^{-3}$ mol) at RT. The homogeneous reaction mixture was then introduced into a J. Young-tap NMR tube and placed in an oil bath heated to 100 °C. The conversion of the reaction was monitored by comparative integration of the signal relative to the olefinic protons of the substrate and the signal relative to the protons of the product. A similar procedure was used for kinetic measurements with precatalysts $\mathbf{3}_{Th,Zr}$/$\mathbf{3'}_{Th,Zr}$ and $\mathbf{4}_{Th,Zr.}$

For cationic complexes $\mathbf{2}_{Zr}$ and $\mathbf{2}_{Hf}$: In an Ar-filled dry box, $[Ph_3C][B(C_6F_5)_4]$ was slowly added to a solution of $\mathbf{1}_{Zr}$ or $\mathbf{1}_{Hf}$ (0.016 mmol) in C_6D_6 (0.6 mL) at RT. The solution was stirred a few minutes and transferred into a vial containing the corresponding aminoalkene (0.16 mmol). The heterogeneous reaction mixture was then introduced into a J. Young-tap NMR tube and placed in an oil bath heated at 100 °C. The conversion of the reaction was monitored by comparative integration of the signal relative to the olefinic protons of the substrate and the signal relative to the protons of the product.

Procedure B: Amido precursors $\mathbf{3}_{Th,M}$/$\mathbf{3'}_{Th,M}$ and $\mathbf{4}_{Th,M}$ (M = Zr, Hf) were tested as catalysts in the intramolecular hydroamination reaction by using a two-necked 10 mL round bottom flask equipped with a magnetic stir bar, a reflux condenser and a septum. In a typical procedure, a solution of the pre-catalyst (5 mol%) in dry and degassed toluene (2.5 mL) was heated at 100 °C. After keeping the pre-heated catalyst solution under stirring for 10 min, a pre-heated (80 °C) solution of the aminoalkene **4** (0.150 g, 0.632 mmol) in dry and degassed toluene (0.5 mL) was added by a syringe in one portion. Afterwards, the reaction course was periodically monitored by sampling the reaction mixture and analyzing it with GC–MS, till completeness was achieved. Finally, the reaction mixture was concentrated under reduced pressure and the crude material was purified by flash-chromatography ($CH_2Cl_2 + 5\%$ MeOH) to give the final pure pyrrolidine.

Kinetic measurements on $\mathbf{3}_{Th,Zr}$/$\mathbf{3'}_{Th,Zr}$ and $\mathbf{4}_{Th,Zr}$

Kinetic studies were performed for the conversion of **4** by varying the catalyst concentration (4, 6, or 8 mol%) or the catalyst precursor ($\mathbf{3}_{Th,Zr}$/$\mathbf{3'}_{Th,Zr}$ or $\mathbf{4}_{Th,Zr}$), for all runs with a constant initial concentration of **4**. All measurements were performed in a sealed J-Young NMR tube and the course of the process was monitored by ^{1}H NMR spectra recorded at constant time intervals with ferrocene as the internal standard. Both catalyst precursors $\mathbf{3}_{Th,Zr}$/$\mathbf{3'}_{Th,Zr}$ and $\mathbf{4}_{Th,Zr}$ showed a first order dependence in substrate consumption/cyclization. To better compare the two catalyst precursors, 5 mol% of $\mathbf{3}_{Th,Zr}$/$\mathbf{3'}_{Th,Zr}$ were compared with 3.75 mol% of the pure $\mathbf{4}_{Th,Zr}$. Previous studies by some of us showed a 25:75 ratio of $\mathbf{3}_{Th,Zr}$/$\mathbf{3'}_{Th,Zr}$ at the target reaction temperature (100 °C).[4] Based on this, equal amounts of the cyclometalated species $\mathbf{3'}_{Th,Zr}$ and $\mathbf{4}_{Th,Zr}$ were then taken into account. In a typical procedure, stock solutions of catalyst precursors $\mathbf{3}_{Th,Zr}$/$\mathbf{3'}_{Th,Zr}$ and $\mathbf{4}_{Th,Zr}$ were prepared by dissolving each complex (20 mg) in [D$_8$]toluene (0.5 mL). **4** (20 mg) and ferrocene (98%, 5 mg, 26.34 μmol) (internal standard)[10j] were weighted into a 1 mL volumetric flask and dissolved in [D$_8$]toluene (≈0.2 mL). Afterwards, a proper amount of the stock solution of the catalyst precursor (0.06 mL of $\mathbf{3}_{Th,Zr}$/$\mathbf{3'}_{Th,Zr}$; 0.04 mL of $\mathbf{VI}_{Th,Zr}$) was added to the 1 mL volumetric flask and the volume was topped to 1 mL with [D$_8$]toluene. The as-prepared solution was shaken and 0.8 mL were rapidly transferred into the J-Young NMR tube. The tube was placed into a pre-heated (100 °C) 300 MHz NMR probe and the system was allowed to thermally equilibrate for 5 min before collecting the $t = 0$ min ^{1}H NMR spectrum. The ^{1}H NMR spectra (8 scans) were collected every 5–10 min up to the almost complete substrate conversion (at least 90%). Comparison of the integration of product and substrate peaks with internal standard peaks was used to calculate the relative percentage of substrate and product at any given time (see the Supporting Information).

First order in catalyst concentration for the pure $\mathbf{4}_{Th,Zr}$ was determined by using a similar procedure to that described above. Three different catalyst concentrations (4, 6 and 8 mol% of $\mathbf{4}_{Th,Zr}$) were used in the presence of a constant concentration of **4**. In a typical procedure, the proper amount of $\mathbf{4}_{Th,Zr}$ in [D$_8$]toluene (stock solution) was added to a solution of **4** (20 mg, 84.27 μmol) and ferrocene (5 mg, 26.34 μmol, internal standard) and the volume was increased to 1 mL with [D$_8$]toluene. The solution was shaken and 0.8 mL were rapidly transferred into the J-Young NMR tube. The reaction course was monitored by ^{1}H NMR spectra, similarly to the procedure described above (see the Supporting Information).

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Keywords: cations · hafnium · hydroamination · nitrogen heterocycles · zirconium

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[20] This co-existence had already been noticed for the benzyl analogue $\{N^-,N,C^-\}N_2^{Fu}Zr(CH_2Ph)_2$,[4b] and in this case it is reasonably caused by the combination of three factors: 1) disorder present on the dimethylamido ligands; 2) the (very) low temperature data collection, and 3) the employ of two-dimensional CCD X-ray detectors.

[21] Although variable temperature ^{1}H NMR spectra of $\mathbf{3}_{\mathrm{Ph,Zr}}$/$\mathbf{3'}_{\mathrm{Ph,Zr}}$ showed the presence at RT of almost exclusively trisamido form ($\mathbf{3}_{\mathrm{Ph,Zr}}$) its isolation in crystals for X-ray diffraction analysis required severe and controlled conditions.

[22] For a comparison of the catalytic performance of our Zr^{IV} and Hf^{IV}-amido catalysts on the model hydroamination/cyclization reaction of **1**, see Refs. [10b,c,g,k,l,m].

[23] The molar fraction of the tris- and bisamido (cyclometalated) species $\mathbf{3}_{\mathrm{Th,Zr}}$/$\mathbf{3'}_{\mathrm{Th,Zr}}$, in toluene at 100 °C was found to be 25:75 mol %.

[24] A zero-order dependence of the hydroamination reaction rate on aminoalkene concentration was also observed with some group IV metal based catalytic systems, see Refs. [10e,x].

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