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ARTICLE

Zirconium Complexes Stabilized by Amine-Bridged Bis(phenolato) Ligands as Precatalysts for Intermolecular Hydroamination Reactions †

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A series of zirconium complexes bearing amine-bridged bis(phenolato) ligands of different steric and electronic properties have been synthesized, and their activities in catalyzing intermolecular hydroamination reactions have been studied and compared. In general, hexacoordinate zirconium dibenzyl complexes **1**-**4** stabilized by [ONNO]- or [ONOO]-type ligands were found to be less active than pentacoordinate complexes **5** and **7** that carry [ONO]-type ligands, which clearly imply that amine-bridged bis(phenolato) ligands play crucial roles in influencing catalytic activities. Complex **5** showed good activities and regioselectivities in catalysing reactions of various primary amines and alkynes. Moreover, reactions of challenging substrates, including secondary amines, internal alkynes, and hydrazines, were achieved with *in situ* generated cationic species from complex **5** and $[Ph_3C][B(C_6F_5)_4]$.

Introduction

Hydroamination reactions are direct addition of N–H bonds across C–C unsaturated bonds, which provide a highly atom economic strategy to prepare compounds containing nitrogen atoms.[1] The transformation can be promoted by a wide range of complexes of transition metals,[2] lanthanides,[1h,3] and main group elements,[1h, 4] which allow these processes to be performed under relatively mild conditions. As one type of low-toxic and easily available metal species, group 4 metal complexes[1c,d,f,h,5,6] have attracted much interest due to their generally high reactivity in catalysing both intra-[5] and intermolecular[6] hydroamination reactions. However, the limitation of group 4 metal catalysed intermolecular hydroamination reactions lies in the narrow substrate scope, which is mainly restricted to primary amines. As an exception, Schafer et al. reported a tethered zirconium bis(ureate) complex which showed good activities in catalysing the hydroamination of aliphatic secondary amines.[6w]

Modification of ligands is a practical strategy to tune the catalytic activities of metal complexes. Bis(phenolato) ligands have been intensively studied, due to their good capacities in stabilizing metal centres, as well as their structural diversity which enables a detailed study on the correlation between structures and catalytic activities of resulting complexes. A wide range of main group and transition metal complexes bearing bis(phenolato) ligands have been synthesized,[7] and are mainly applied in promoting ring-opening polymerization of olefin,[7c-k] lactide,[7l-s] epoxide,[7t-u] and some other monomers.[7v-x] Recently, we reported a zirconium complex stabilized by an [ONNO]-type tetradentate ligand, which was found to be a good precatalyst for intermolecular hydroamination reactions of primary amines in the presence of cationic reagent $[Ph_3C][B(C_6F_5)_4]$.[8] However, it failed to catalyze reactions with secondary amines. In remarkable contrast, a zirconium complex bearing an [ONO]-type tridentate ligand proved efficient in catalysing intermolecular hydroamination reactions of secondary amines.[9] Apparently, a small change in ancillary ligands leads to significant differences in catalytic performance of complexes. We thus extended our investigations to a series of bis(phenolato) ligands of different steric and electronic properties, and carried out a systematic study on their influence on complex formation and catalytic activities of resulting complexes.

Results and discussion

Synthesis of zirconium complexes.

Amine-bridged bis(phenol) $\mathbf{L^1H_2}$ – $\mathbf{L^4H_2}$ bearing coordinating sidearms were synthesized (Figure 1), with the fourth donor being nitrogen or oxygen atoms. Precursors $\mathbf{L^5H_2}$ – $\mathbf{L^7H_2}$ of potentially tridentate ligands carrying non-coordinating sidearms were also prepared. Moreover, different substituents on phenyl rings, including methyl, *tert*-butyl and cumyl groups, were introduced to exert different spatial environments for

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†Electronic supplementary information: X-ray crystallographic data for **6** (CCDC 1410748) in CIF format, ^{1}H and ^{13}C NMR spectra of complexes **2**, **3**, **6**, **7** and hydroamination products and ^{1}H NMR spectra for kinetic studies.

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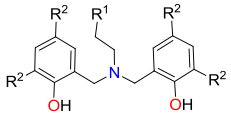
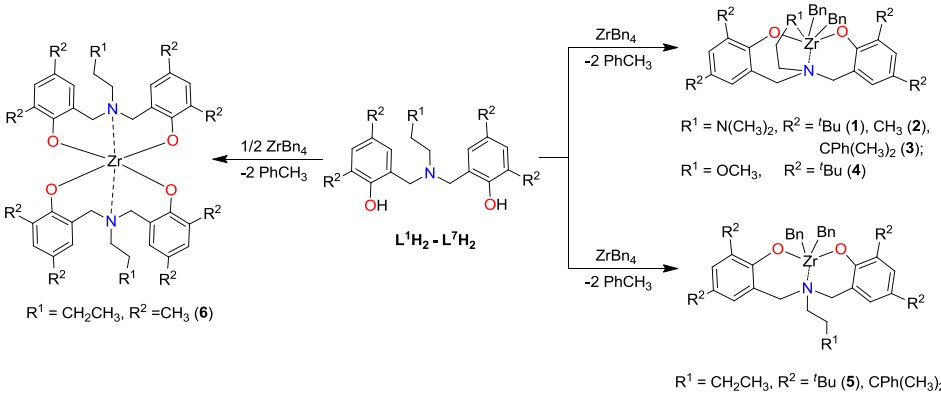
metal centers. All ligand precursors were synthesized through Mannich condensation reactions from readily available starting materials, namely primary amines, formaldehyde, and substituted phenols.[10]



$R^1 = N(CH_3)_2$, $R^2 = {}^t$Bu ($\mathbf{L^1H_2}$), CH_3 ($\mathbf{L^2H_2}$), $CPh(CH_3)_2$ ($\mathbf{L^3H_2}$);
$R^1 = OCH_3$, $R^2 = {}^t$Bu ($\mathbf{L^4H_2}$);
$R^1 = CH_2CH_3$, $R^2 = {}^t$Bu ($\mathbf{L^5H_2}$), CH_3 ($\mathbf{L^6H_2}$), $CPh(CH_3)_2$ ($\mathbf{L^7H_2}$)

Figure 1. Ligand precursors

Metathesis reactions of $ZrBn_4$ and bis(phenol) at room temperature provide an easy access to zirconium dialkyl complexes. Complexes **1**-**5**, and **7** were isolated as expected in 90-95% yields (Scheme 1). However, the reaction of *n*-butylamine-bridged bis(phenol) $\mathbf{L^6H_2}$ carrying methyl substituents with $ZrBn_4$ in 1:1 ratio gave rise to homoleptic zirconium complex **6** in 49% yield accompanied with unreacted $ZrBn_4$. Various reaction conditions, including different ratios of starting materials, different sequences of reactant addition, and different temperatures (r.t. or -78 °C), resulted in complex **6** as the sole product. Reaction of the correct stoichiometry at room temperature led to an almost quantitative yield of 97%. The formation of the homoleptic complex may be ascribed to two reasons: 1) the sterically less-hindered methyl substituents on phenyl rings; 2) the absence of the fourth coordinating site from the bis(phenolato) ligand.[11] ^{1}H NMR spectrum of complex **6** shows signals corresponding to one set of ligand $\mathbf{L^6}$, revealing a symmetric structure.



Scheme 1. Synthesis of zirconium complexes

Solid state structure of **6** (depicted in Figure 2) obtained from X-ray diffraction analyses on single crystals supports that the two amine-bridged bis(phenolato) ligands coordinate to the metal center through two N and four O donors. The overall coordination geometry is octahedral.

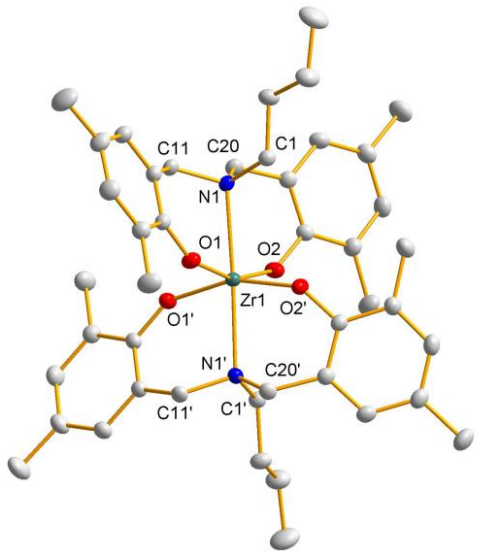


Figure 2. Molecular structure of **6**·$PhCH_3$ showing 30% probability ellipsoids; hydrogen atoms and solvent molecules are omitted for clarity. A summary of crystallographic data is given in ref.12. Selected bond lengths (Å) and bond angles (deg): Zr1-O1 2.0014(15), Zr1-O2 1.9941(15) Zr(1)-N(1) 2.4197(17); O(2)-Zr(1)-O(2') 91.50(10), O(2)-Zr(1)-O(1) 159.47(6), O(2')-Zr(1)-O(1) 91.30(7), O(1)-Zr(1)-O(1') 93.17(9), O(2)-Zr(1)-N(1) 80.42(6), O(2')-Zr(1)-N(1) 101.30(6), O(1)-Zr(1)-N(1) 79.09(6), O(1)-Zr(1)-N(1') 99.22(6), N(1)-Zr(1)-N(1') 177.58(8), C(5)-O(1)-Zr(1) 144.30(13), C(14)-O(2)-Zr(1) 138.53(14), C(1)-N(1)-C(11) 112.24(17), C(1)-N(1)-C(20) 111.91(16), C(11)-N(1)-C(20) 105.59(16), C(1)-N(1)-Zr(1) 108.64(12), C(11)-N(1)-Zr(1) 107.61(12), C(20)-N(1)-Zr(1) 110.77(13), N(1)-C(1)-C(2) 117.36(18).

Hydroamination reactions of alkynes and primary amines.

Catalytic behaviors of complexes **1**-**7** were evaluated and compared in catalyzing the hydroamination reaction between aniline and phenylacetylene (Table 1). Analogous to the previously reported zirconium amide stabilized by the same ligand $\mathbf{L^1}$,[8] complex **1** failed to catalyze this transformation at 110 °C (Table 1, entry 1). Similarly, complexes **2** and **3** carrying different substituents on phenyl rings showed no activity (entry 2 and 3). Changing the tetradentate [ONNO]-type bis(phenolato) ligand to [ONOO]-type ligand $\mathbf{L^4}$ proved not helpful, as complex **4** did not show any activity under identical conditions (entry 4). In contrast, mixtures of complexes **1**-**4** and $[Ph_3C][B(C_6F_5)_4]$ (TB) efficiently catalyzed the reaction, and led to the desired product **10a** in almost quantitative yields (entry 5-8) within a short period of 1-2 h. Cationic species derived from reactions of **1**-**4** with TB are believed to play

crucial roles in catalyzing this transformation, which may be attributed to the enhanced Lewis acidity of metal centers, as well as larger coordination sites for the substrates.[8] Moreover, Markovnikov products formed exclusively, revealing 100% regioselectivity of these reactions.

In stark contrast to the above-discussed findings, the pentacoordinate complex **5** itself worked well in catalyzing the reaction between aniline and phenylacetylene, and 98% of the expected product **10a** formed (entry 9). It is noteworthy that 21% of Z-enyne **11a** resulting from the dimerization of phenylacetylene was isolated as well (entry 9). The sequence of starting material addition proved crucial in determining product distributions. If alkyne was mixed with the precatalyst **5** followed by the addition of amine, hydroamination reaction occurred exclusively (entry 10), while the reversed sequence led to a mixture of **10a** and **11a** (entry 9). Reactions of phenylacetylene and aniline in the ratio of 2:1 gave the same trends (entry 11 and 12). This finding resembles that reported by Schafer et al., which discloses that a dibenzyl tethered bis(ureate) zirconium precatalyst in the presence of aniline efficiently catalyzed the dimerization of phenylacetylene.[13] Changing the ratio of starting materials to 1:1 resulted in 96% and 97% yields of **10a** in either chlorobenzene (entry 13) or toluene (entry 14). The homoleptic complex **6** proved inactive in catalyzing this reaction (entry 15), while complex **7** showed similar activity to that of **5** (entry 16). The activity differences between hexacoordinate complexes **1**-**4** and pentacoordinate complexes **5** and **7** clearly reveal the important role of bis(phenolato) ligands in influencing the catalytic activities of respective complexes. The absence of the fourth coordination site in complexes **5** and **7** makes the metal centers more Lewis acidic and renders coordination sites for substrates to bind, which may be the major reasons that are responsible for enhanced activities of pentacoordinate complexes. This finding is different from previous reports by Kol, Goldschmidt and co-workers, in which hexacoordinate complexes are found to be more active than pentacoordinate counterparts in initiating the polymerization of 1-hexene.[10] Borates $[Ph_3C][B(C_6F_5)_4]$ (TB), $[PhMe_2NH][B(C_6F_5)_4]$, and $[Et_3NH][BPh_4]$ have been tested in the absence of zirconium complexes, and no desired product was detected (entry 17-19), which verifies the essential role of zirconium complexes in catalyzing the transformation.

Table 1. Hydroamination/reduction reactions of aniline and phenylacetylene catalyzed by different complexes[a]

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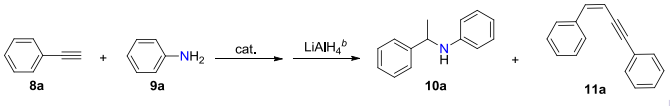

entry	cat.	8a:9a	solvent	time (h)	yield of **10a** (%)[c]	yield of **11a** (%)[c]
1	**1**	1.5:1	PhCl	12	trace	trace
2	**2**	1.5:1	PhCl	12	trace	trace
3	**3**	1.5:1	PhCl	12	trace	trace
4	**4**	1.5:1	PhCl	12	trace	trace
5	**1** + TB	1.5:1	PhCl	1	>99	trace
6	**2** + TB	1.5:1	PhCl	1	>99	trace
7	**3** + TB	1.5:1	PhCl	2	>99	trace
8	**4** + TB	1.5:1	PhCl	1	>99	trace
9	**5**	1.5:1[d]	PhCl	4	98	21[f]
10	**5**	1.5:1[e]	PhCl	4	98	3[f]
11	**5**	2:1[d]	PhCl	4	96	49[f]
12	**5**	2:1[e]	PhCl	4	96	4[f]
13	**5**	1:1[e]	PhCl	4	96	trace
14	**5**	1:1[e]	Tol	4	97	trace
15	**6**	1:1[e]	Tol	12	trace	trace
16	**7**	1:1[e]	Tol	8	98	trace
17	TB	1:1[e]	PhCl	12	trace	trace
18	$[PhMe_2NH][B(C_6F_5)_4]$	1:1[e]	PhCl	12	trace	trace
19	$[Et_3NH][BPh_4]$	1:1[e]	PhCl	12	trace	trace

[a] Conditions unless otherwise stated: precatalyst (0.1 mmol), $[Ph_3C][B(C_6F_5)_4]$ (TB), (0.1 mmol) if necessary, **8a** (desired amount) and **9a** (0.091 mL,1 mmol) was added successively into chlorobenzene (2 mL), and the mixture was heated at 110 °C for desired time. [b] The initially formed imine was reduced by $LiAlH_4$ to give corresponding secondary amines. [c] Isolated yield. No anti-Markovnikov product was detected. [d] **9a** was mixed with **5** in solution for 1 h followed by the addition of **8a**. The mixture was heated for another 3 h. [e] **8a** was mixed with **5** in solution for 1 h followed by the addition of **9a**. The mixture was heated for another 3 h. [f] Yield is based on **9a**.

Complex **5** was then tested in catalysing the intermolecular hydroamination reactions between various alkynes and aniline (Chart 1). Excellent yields of 94-99% were obtained from reactions of phenylacetylene derivatives bearing either electron-withdrawing or donating groups at *ortho*-, *meta*-, or *para*-positions (**10b**-**f**). The reaction with 2-ethynylthiophene also proceeded smoothly, and afforded the desired product **10g** in 96% yield. Aliphatic alkynes, including 3-phenyl-1-propyne, 1-hexyne, and cyclohexylacetylene, reacted straightforwardly with aniline under optimal conditions, and gave rise to secondary amines **10h**-**j** after reduction in almost quantitative yields of 95-99%. All products **10b**-**j** formed following Markovnikov rules.

For reactions of internal alkynes catalysed by complex **5**, no conversion was detected at all after 12 h of reaction at 110 °C. However, *in situ* generated cationic species from complex **5** and $[Ph_3C][B(C_6F_5)_4]$ (TB) efficiently catalysed reactions between aniline and diphenylacetylene or 1-phenyl-1-propyne, and afforded the desired products in 93% (**10k**) and 89% (**10l** + **10l'**) yields, respectively. It is noteworthy that for the unsymmetrical substrate 1-phenyl-1-propyne, a mixture of **10l** and **10l'** resulting from different directions of the addition reaction was obtained.

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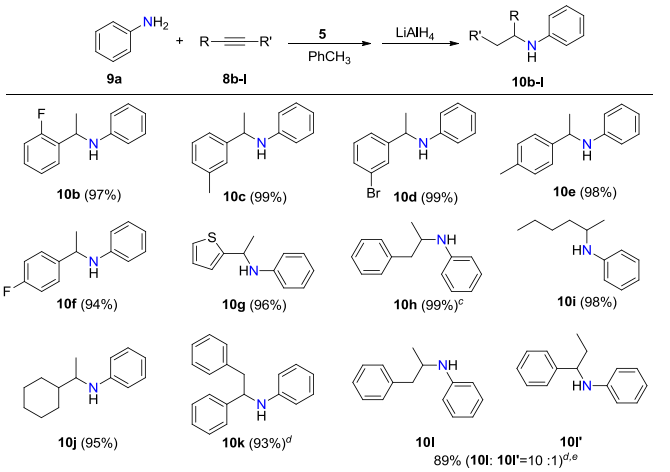
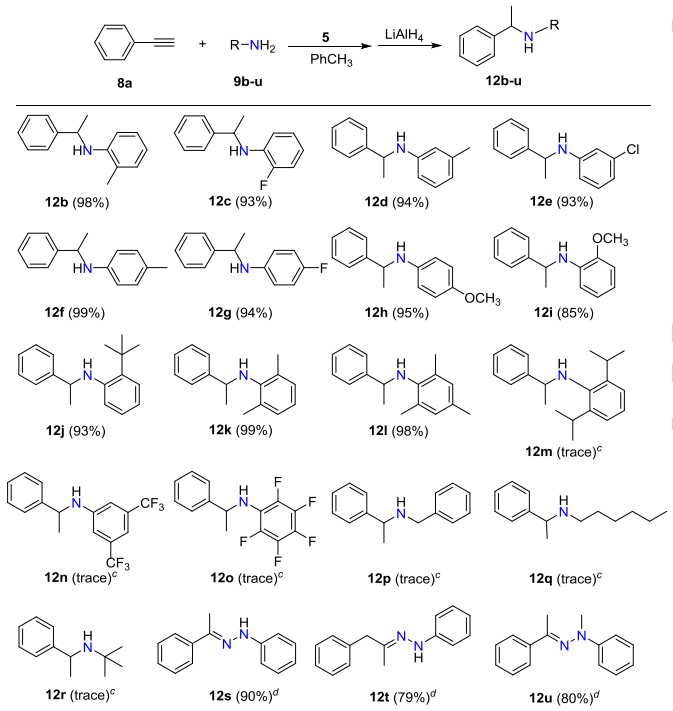
Chart 1. Hydroamination/reduction reactions of aniline and various alkynes catalyzed by **5**[a,b]



[a] Conditions unless otherwise stated: **8** (1 mmol) was mixed with **5** (0.070 g, 0.1 mmol) in toluene (2 mL) for 1 h followed by the addition of **9a** (0.091 mL, 1 mmol). The mixture was heated at 110 °C for another 3 h. [b] Isolated yield. [c] The alkyne is 3-phenyl-1-propyne. [d] In the presence of TB in PhCl. [e] The alkyne is 1-phenyl-1-propyne.

Hydroamination reactions between phenylacetylene and various anilines catalyzed by complex **5** have also been studied, and results are summarized in Chart 2. For mono-substituted anilines, good yields of 85-99% were obtained (**12b**-**j**), regardless there are *ortho*-, *meta*-, or *para*- substitutes which are electron-withdrawing or donating. It is noteworthy that reactions with 4- and 2-anisidines that contain coordinating oxygen atoms proceeded smoothly, and generated the desired products in 95% (**12h**) and 85% (**12i**) yields, respectively. No significant catalyst deactivation was observed. For comparison, a much lower yield (11%) of **12h** was obtained from the reaction catalyzed by cationic species, probably due to the stronger binding of the substrate with the more Lewis acidic center that leads to deactivation of catalytically active species.[8] 2-*tert*-butylaniline that carries a bulky *ortho*-substituent reacted with phenylacetylene under optimal conditions, and afforded **12o** in 93% yield. For anilines that bear more than one substituent, their reactions with phenylacetylene led to different results. Reactions with 2,6-dimethylaniline and 2,4,6-trimethylaniline worked straightforwardly, and afforded desired products in 99% (**12k**) and 98% (**12l**) yields, respectively. As the substituents get bulkier, no product was detected from the reaction with 2,6-diisopropylaniline (**9m**). No reaction occurred with aniline bearing more than one electron-withdrawing group, i.e., 3,5-bis(trifluoromethyl)aniline (**9n**) and pentafluoroaniline (**9o**), even after prolonged reaction time. Complex **5** also failed to catalyze reactions involving primary aliphatic amines such as benzylamine (**9p**), hexylamine (**9q**) and *tert*-butyl amine (**9r**). Reactions with substrates **9n**-**r** have also been tested in the presence of TB, however, to no avail. Hydrazines have also been studied in reactions with phenylacetylene and 3-phenyl-1-propyne. No reaction occurred in the absence of TB, while good yields of 79-90% (**12s**-**u**) were obtained in the presence of TB.

Chart 2. Hydroamination/reduction reactions of phenylacetylene and various amines catalyzed by complex **5**[a,b]



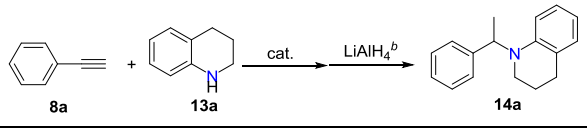
[a] Conditions unless otherwise stated: **8a** (0.11 mL, 1 mmol) was mixed with **5** (0.070 g, 0.1 mmol) in toluene (2 mL) for 1 h followed by the addition of **9** (1 mmol). The mixture was heated at 110 °C for another 3 h. [b] Isolated yield. [c] 24 h reaction time. [d] In the presence of TB in PhCl.

Hydroamination reactions of alkynes and secondary amines.

As previously communicated, the mixture of complex **5** and TB showed good activities in catalyzing the reaction of secondary amines and alkynes, which is the first group 4 metal based catalyst in mediating intermolecular hydroamination reactions of amines bearing both aryl and alkyl *N*-substituents.[9] A comparative study with other complexes revealed that mixtures of complexes **1-4** and TB failed to catalyze hydroamination reactions of 1,2,3,4-tetrahydroquinoline (Table 2, entry 1-4). Complex **5** itself did not catalyze this transformation (entry 5), which is different from the result obtained in the presence of TB (entry 6). The homoleptic complex **6** proved inactive (entry 7), and complex **7** showed similar activity as that of **5** (entry 8). These findings are consistent with those of primary amines (*vide supra*) that enhanced Lewis acidities of metal centers and suitable coordination sites for substrates to bind are essential for complexes of higher activities in catalyzing hydroamination reactions, which can be achieved by modification of the amine-bridged bis(phenlato) ligands. Similarly, borates showed negligible activities in catalyzing the hydroamination reactions of secondary amines (entry 9-11) (*vide supra*). As complex **5** exhibited limited activity in catalyzing reactions of aliphatic

secondary amines,[9] complex **7** was tested in catalyzing reactions of pyrrolidine, piperidine, 1,2,3,4-tetrahydroisoquinoline and morpholine with phenylacetylene. However, no desired product was detected.

Table 2. Hydroamination/reduction reactions of 1,2,3,4-Tetrahydroquinoline and phenylacetylene catalyzed by different complexes[a]



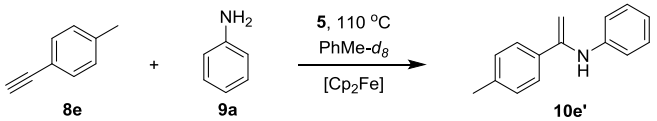
entry	cat.	8a:13a	solvent	time (h)	yield of **14a** (%)[c]
1	**1** + TB	2:1	PhCl	12	trace
2	**2** + TB	2:1	PhCl	12	trace
3	**3** + TB	2:1	PhCl	12	trace
4	**4** + TB	2:1	PhCl	4	trace
5	**5**	2:1	Tol	8	trace
6	**5** + TB	2:1	PhCl	4	90
7	**6** + TB	2:1	PhCl	12	0
8	**7** + TB	2:1	PhCl	6	87
9	TB	2:1	PhCl	12	trace
10	$[PhMe_2NH][B(C_6F_5)_4]$	2:1	PhCl	12	10
11	$[Et_3NH][BPh_4]$	2:1	PhCl	12	trace

[a] Conditions unless otherwise stated: Catalyst (0.1 mmol), $[Ph_3C][B(C_6F_5)_4]$ (TB) (0.1 mmol) if necessary, **13a** (0.125mL, 1 mmol), **8a** (0.22 mL, 2 mmol), solvent (2 mL), 110 °C. [b] The initially formed enamine was reduced by $LiAlH_4$ to give corresponding tertiary amines. [c] Isolated yield. No anti-Markovnikov product was detected.

Kinetic study.

Kinetic study was conducted in order to gain further insights into the catalytic process. As previously reported, the reaction of primary amines which is catalyzed by cationic zirconium complex stabilized by ligand **L**[1] showed first order dependence on [alkyne], while a reversed-first order dependence on [amine].[8] The behavior of complex **5** was then investigated and compared.

The kinetic experiment was carried out with ten-fold of aniline **9a** under pseudo-first order conditions, and the concentration of *p*-tolylacetylene **8e** was monitored as a function of time by ^{1}H NMR spectroscopy (Scheme 2). A representative plot of ln([**8e**]$_0$/[**8e**]) versus time shows a first-order disappearance (Figure 3).[6p,q, 14] Meanwhile, the concentration of amine (1, 2 and 10 equiv.) did not influence the reaction rate, suggesting a zero-order dependence on amines. Overall, the rate law is deduced as $v \sim [\text{alkyne}]^1[\text{amine}]^0$. The different order of [amine] comparing to that of cationic species catalyzed system may be ascribed to the stronger binding of amine to more Lewis acidic metal centers in the latter, which shuts down the catalytic cycle for certain extent.



Scheme 2. Model Reaction for Kinetic Study of Complex **5**.

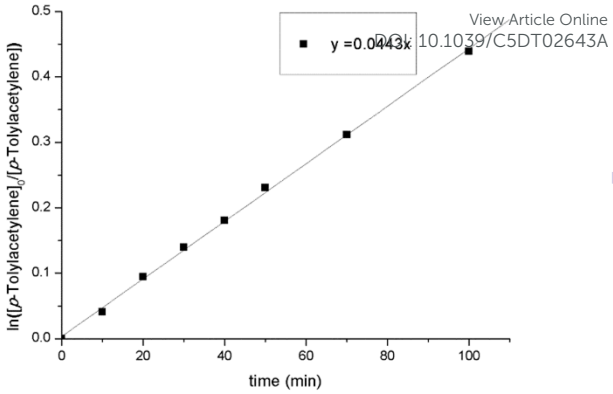


Figure 3. Plot of ln[**8e**]$_0$/[**8e**] versus time (s) for the hydroamination reaction of *p*-tolylacetylene **8e** and aniline **9a** catalyzed by 10 mol% of complex **5**. Conditions: [**8e**]$_0$ = 0.3636 mol·L^{-1}, [**9a**]$_0$ = 3.6374 mol·L^{-1}; 10 mol% of complex **5**, $PhCH_3$-d_8, 110 °C.

Plausible mechanism.

Based on the above-discussed experimental findings, a plausible mechanism has been proposed. Since the mechanism of cationic species catalysed transformations has been communicated,[9] only the mechanism of neutral complexes catalysed reactions is depicted in Figure 4. An imido intermediate **A** has been proposed, which explains why neutral complexes failed to catalyse hydroamination reactions of secondary amines. Coordination of alkynes took place, followed by the [2 + 2] cycloaddition and aminolysis, which gave rise to hydroamination products. Meanwhile, a zirconium alkynyl species **E** may form, which led to the dimerization of phenylacetylene.[13]

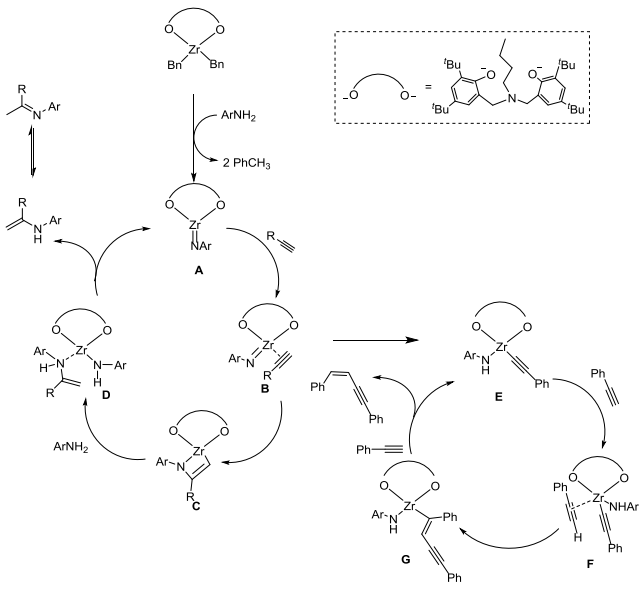


Figure 4. A plausible mechanism.

Conclusions

In summary, a series of zirconium complexes stabilized by amine-bridged bis(phenolato) ligands have been prepared, and

their behaviors in catalyzing intermolecular hydroamination reactions have been studied and compared. Hexacoordinate zirconium complexes **1**-**4** bearing either [ONNO]- or [ONOO]-type ligands were found to be less active than pentacoordinate complexes **5** and **7** bearing [ONO]-type ligands, revealing the important role that ligands play in influencing catalytic activities. Complex **5** efficiently catalyzed the intermolecular hydroamination reactions of various primary amines and alkynes, and showed good regiocontrol. Reactions of challenging substrates, such as internal alkynes, hydrazines, and secondary amines, were achieved with *in situ* generated cationic species from complex **5** and $[Ph_3C][B(C_6F_5)_4]$. Further study on development of group 4 metal complexes as precatalysts in catalyzing atom economic transformations is on-going in our laboratory

Experimental section

General considerations.

All manipulations of air- and/or moisture-sensitive compounds were performed under nitrogen atmosphere using standard Schlenk or glovebox techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL 400 MHz spectrometer. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. X-ray crystallographic data were collected using a Bruker AXS D8 X-ray diffractometer. Toluene and hexane were freshly distilled by refluxing over sodium/benzophenone ketyl and distilled prior to use. C_6H_5Cl, C_6D_6, PhMe-d_8 and C_6D_5Cl were degassed and distilled over CaH_2. $[Ph_3C][B(C_6F_5)_4]$ purchased from Strem Chemicals, Inc. was used without purification. $ZrBn_4$ and ligand precursors $\mathbf{L^1H_2}$ - $\mathbf{L^7H_2}$ were prepared according to reported procedures.[10] Compounds **1**, **4**, **5** and all of hydroamination products were confirmed by comparing ^{1}H NMR spectra with literature data.[8,9,10,15] Amines were distilled over CaH_2. Alkynes were degassed, flushed with argon and stored over molecular sieves (4 Å).

General procedure for zirconium complexes synthesis.[10]

To a solution of $ZrBn_4$ (3 mmol) in toluene (10 mL) was added dropwise $\mathbf{L^nH_2}$ (n = 1-5 and 7) (3 mmol) or $\mathbf{L^6H_2}$ (6 mmol) in toluene (5 mL) at room temperature over 15 min. After stirring for 12 hours at room temperature, toluene was removed under reduced pressure and the residue was washed with hexane (2 × 5 mL). Complexes **1**-**4** were recrystallized from toluene solution, while complexes **5**-**7** were recrystallized from toluene and hexane solution. Complexes **1** - **4** were obtained as yellow solids, and **5**-**7** were obtained as colourless solids.

$ZrBn_2L^2$ (2). Complex **2** was isolated in 1.70 g (90% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.54-7.52 (d, 2H, *J* = 13.1 Hz, Ar-H), 7.05-7.01 (m, 2H, Ar-H), 7.34-7.31 (m, 2H, Ar-H), 6.95-6.88 (m, 7H, Ar-H), 6.66-6.63 (m, 1H, Ar-H), 6.52 (s, 2H, Ar-H), 3.61-3.57 (d, 2H, *J* = 13.48 Hz, $ArCH_2$), 2.65(s, 2H, $PhCH_2$), 2.48-2.45 (d, 2H, *J* = 11.68Hz, $PhCH_2$), 2.45(s, 6H, *p*-$PhCH_3$), 2.41(s, 2H, $PhCH_2$), 2.20(s, 6H, *o*-$PhCH_3$), 1.87 (m, 2H, NCH_2C), 1.54 (s, 6H, $N(CH_3)_2$), 1.27(m, 2H, CCH_2N). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6):156.7, 149.6, 146.2, 131.9, 128.0, 128.2, 128.1, 127.9, 126.7, 125.0, 122.0, 119.9 (Ar-C), 65.5 ($ArCH_2N$), 63.5 ($ArCH_2N$), 59.7($PhCH_2$), 50.8($PhCH_2$), 31.6(NCH_2CH_2N), 22.7(NCH_2CH_2N), 20.4 (*p*-$PhCH_3$), 16.3 (*o*-$PhCH_3$), 14.0 ($N(CH_3)_2$). Anal. Calcd for $C_{36}H_{44}N_2O_2Zr$: C, 68.85; H, 7.06; N, 4.46. Found: C, 68.83; H, 7.01; N, 4.49

$ZrBn_2L^3$ (3). Complex **3** was isolated in 2.88 g (92% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.66-7.59 (m, 4H, Ar-H), 7.40 (m, 9H, Ar-H), 7.26-7.01 (m, 16H, Ar-H), 6.68-6.62 (m, 4H, Ar-H), 6.50-6.47 (m, 1H, Ar-H), 6.14-6.13 (m, 2H, Ar-H), 2.92-2.89 (d, 2H, *J* = 13.08Hz, $ArCH_2$), 2.47 (s, 2H, $PhCH_2$), 2.29 (s, 2H, $PhCH_2$), 2.21-2.18 (d, 2H, *J* = 13.48Hz, $ArCH_2$), 1.98 (s, 6H, *p*-$PhCH_3$), 1.87 (s, 6H, *o*-$PhCH_3$), 1.68 (s, 12H, $PhCH_3$), 1.68 (m, 2H, NCH_2C), 1.68 (m, 2H, CCH_2N), 1.37 (s, 6H, $N(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): 156.9, 150.7, 150.3, 148.5, 145.6, 139.9, 135.4, 127.8, 127.5, 126.7, 126.3, 126.0, 125.9, 125.2, 125.0, 120.5, 119.6, (Ar-C), 70.6 ($ArCH_2N$), 66.6 ($ArCH_2N$), 63.7 ($PhCH_2$), 59.1 ($PhCH_2$), 41.9 (*p*-$PhCH_3$), 31.1 (NCH_2CH_2N), 30.7 (NCH_2CH_2N), 30.6 (*o*-$PhCH_3$), 28.8 ($N(CH_3)_2$). Anal. Calcd for $C_{68}H_{76}N_2O_2Zr$: C, 78.19; H, 7.33; N, 2.68. Found: C, 78.22; H, 7.31; N, 4.27

$Zr(L^6)_2$ (6). Complex **6** was isolated in 2.78 g (97% yield) ^{1}H NMR (400 MHz, C_6D_6): δ 7.16-7.12 (m, 4H, Ar-H), 7.07-7.05 (m, 2H, Ar-H), 7.02-7.01 (m, 4H, Ar-H), 6.96-6.92 (m, 4H, Ar-H), 6.83-6.81 (m, 4H, Ar-H), 4.69-4.64 (m, 4H, $ArCH_2$), 3.43-3.37 (t, 4H, NCH_2), 2.88-2.84 (m, 4H, $ArCH_2$), 2.29 (s, 6H, *p*-$PhCH_3$), 2.26 (s, 6H, *p*-$PhCH_3$), 2.26 (s, 6H, *o*-$PhCH_3$), 2.21 (s, 6H, $PhCH_3$), 1.95 (s, 6H, *o*-$PhCH_3$), 1.41-1.37 (m, 4H, $NCCH_2$), 0.83-0.69 (m, 4H, $NCCCH_2$), 0.55-0.51 (m, 6H, $NCCCCH_3$).$^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): 158.1, 158.0, 137.5, 131.8, 129.0, 128.2, 126.4, 126.0, 125.3, 124.8, 124.7, 122.1, 121.9 (Ar-C), 58.4, 58.0 ($ArCH_2N$), 45.9 ($NCCH_2$), 21.1($ArCH_3$), 20.6($PhCH_3$), 20.5, 19.7 ($ArCH_3$), 16.4 ($NCH_2\mathit{CH_2}$), 16.1 ($NCH_2CH_2\mathit{CH_2}$), 13.1 ($NCH_2CH_2CH_2\mathit{CH_2}$). Anal. Calcd for $C_{44}H_{58}N_2O_4Zr{\cdot}2PhCH_3$: C, 72.99; H, 7.82; N, 2.94. Found: C, 73.14; H, 7.90; N, 2.88.

$ZrBn_2L^7$ (7). Complex **7** was isolated in 2.78 g (90% yield). ^{1}H NMR (400 MHz, C_6D_6): δ 7.60-7.59 (m, 2H, Ar-H), 7.34-7.32 (m, 4H, Ar-H), 7.30-7.27 (m, 4H, Ar-H), 7.19-7.00 (m, 16H, Ar-H), 6.91-6.89 (m, 2H, Ar-H), 6.70-6.67 (m, 4H, Ar-H), 6.45-6.43 (m, 2H, Ar-H), 2.98-2.94 (d, 2H, *J* = 13.8Hz, $ArCH_2$), 2.57-2.54 (d, 2H, *J* = 13.92Hz, $ArCH_2$), 1.94 (s, 6H, *p*-$PhCH_3$), 1.80 (s, 6H, *o*-$PhCH_3$), 1.85(s, 2H, $PhCH_2$), 1.83-1.80 (m, 2H NCH_2), 1.67 (s, 12H, $PhCH_3$), 1.55 (s, 2H, $PhCH_2$), 0.77-0.71 (m, 2H, $NCCH_2$), 0.57-0.52(m, 5H, $NCCCH_2CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): 157.3, 156.5, 151.2, 150.7, 150.4, 149.0, 146.0, 140.3, 135.9, 128.3, 128.0, 127.1, 126.8, 126.5, 125.7, 125.5, 121.0, 120.0 (Ar-C), 71.1 ($ArCH_2N$), 61.1 ($ArCH_2N$), 64.1 ($PhCH_2$), 59.5 ($PhCH_2$), 50.2 (NCH_2), 31.6 (*p*-$PhCH_3$), 31.2 ($NCH_2\mathit{CH_2}$), 29.3 ($NCH_2CH_2\mathit{CH_2}$), 22.7 ($PhCH_3$), 14.0 ($NCH_2CH_2CH_2\mathit{CH_2}$). Anal. Calcd for $C_{68}H_{75}NO_2Zr$: C, 79.33; H, 7.34; N, 1.36. Found: C, 79.29; H, 7.31; N, 1.30.

General procedure for hydroamination reactions of primary amines catalyzed by 5.[8]

In a glovebox filled with nitrogen, **8** (1 mmol) was mixed with the toluene solution (2 mL) of **5** (78 mg, 0.1 mmol) for 1 h, followed by the addition of **9** (1mmol). The resulting mixture was stirred at 110 °C for the desired time. After the mixture was cooled to 0 °C, $LiAlH_4$ (76 mg, 2 mmol) was added, and the resulting mixture was stirred at 60 °C for 2 hours. The reaction was quenched by the aqueous solution of NaOH (6 M). The

product was extracted with toluene (3 × 1 mL). All amines shown in Chart 1-2 were isolated by column chromatography (petroleum ether/ethyl acetate =100/1, Al_2O_3) as viscous colorless oil and characterized by ^1H and ^{13}C NMR spectroscopy.

General procedure for hydroamination reactions of secondary amines catalyzed by 5.[9]

In a glovebox filled with nitrogen, PhCl solution (1 mL) of $[Ph_3C][B(C_6F_5)_4]$ (92 mg, 0.01 mmol) was added to PhCl solution (2 mL) of **5** (70 mg, 0.01 mmol) under stirring. A color change from orange to colorless was observed immediately. After 5 min, **13a** (0.125mL, 1 mmol) and **8a** (0.22 mL, 2 mmol) were added to the mixture successively. The resulting solution was stirred at 110 °C for the desired time. After the mixture was cooled to 0 °C, $LiAlH_4$ (76 mg, 2 mmol) was added, and the resulting mixture was stirred at 60 °C for 2 hours. The reaction was quenched by the aqueous solution of NaOH (6 M).The product was extracted with toluene (3 × 1 mL). The crude product obtained after removal of solvent was isolated by column chromatography (petroleum ether, silica gel, 0.5% NEt_3) as viscous colorless oil and characterized by ^1H and ^{13}C NMR spectroscopy

X-Ray crystallographic structure determination.

Suitable single crystals of complex **6** were sealed in a thin-walled glass capillary for determination the single-crystal structures. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo-Kα radiation (λ= 0.71070 Å). The diffracted intensities were corrected for Lorentz/ polarization effects and empirical absorption corrections.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$.The hydrogen atoms in these complexes were generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using *SHELEXL-97* programs.

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Notes and references

1 (a) T. E. Müller and M. Beller, *Chem. Rev.,* 1998, **98**, 675. (b) F. Alonso, I. P. Beletskaya, M. Yus, *Chem. Rev.,* 2004, **104**, 3079. (c) S. Doye, *Synlett,* 2004, 1653. (d) Odom A. L. *Dalton Trans.,* **2005**, 225. (e) R. Severin, and S. Doye, *Chem. Soc. Rev.,* 2007, **36**, 1407. (f) A. V. Lee and L. L. Schafer, *Eur. J. Inorg. Chem*., 2007, 2243. (g) T. E. Müller, K. C. Hultzsch, M. Yus, F. Foubelo, M. Tada, *Chem. Rev*., 2008, **108**, 3795. (h) L. R. Alexander, K. C. Hultzsch, *Top Organomet. Chem*., 2013, **43**, 51.

2 (a) N. Nishina, Y. Yamamoto, *Top Organomet. Chem.* 2013, **43**, 115 and references therein. (b) S. Werkmeister, S. Fleischer, S. Zhou, K. Junge, M. Beller, *ChemSusChem,* 2012, **5**, 777.

3 S. Hong, T. J. Marks, *Acc. Chem. Res*., 2004, **37**, 673.

4 (a) M. R. Crimmin, I. J. Casely and M. S. Hill, *J. Am. Chem. Soc.,* **2005**, *127*, 2042. (b) F. Hild and S. Dagorne, *Organometallics,* 2012, **31**, 1189. (c) C. Brinkmann, A. G. M. Barrett, M. S. Hill and P. A. Procopiou, *J. Am. Chem. Soc.,* 2012, **134**, 2193.

5 Selective reports on group 4 metal complexes catalyzed intramolecular hydroamination reactions: (a) P. L. McGrane, M. Jensen, T. Livinghouse, *J. Am. Chem. Soc.,* 1992, **114**, 5459. (b) P. L. McGrane, T. Livinghouse, *J. Org. Chem.,* 1992, **57**, 1323. (c) H. Kim, P. H. Lee, T. Livinghouse, *Chem. Commun*., 2005, 5205. (d) J. A. Bexrud, J. D. Beard, D. C. Leitch, L. L. Schafer, *Org. Lett*., 2005, **7**, 1959. (e) E. Chong, S. Qayyum, L. L. Schafer, R. Kempe, *Organometallics,* 2006, **25**, 6125. (f) K. Born, S. Doye, *Eur. J. Org. Chem*., 2012, 764. (g) R. K. Thomson, J. A. Bexrud, L. L. Schafer, *Organometallics,* 2006, **25**, 4069. (h) B. D. Stubbert, T. J. Marks, *J. Am. Chem. Soc.,* 2007, **129**, 6149. (i) J. Cho, T. K. Hollis, T. R. Helgert, E. J. Valente, *Chem. Commun*., 2008, 5001. (j) C. Müller, W. Saak, S. Doye, *Eur. J. Org. Chem.,* 2008, 2731. (k) J. A. Bexrud, L. L. Schafer, *Dalton Trans.,* 2010, **39**, 361. (l) D. C. Leitch, R. H. Platel, L. L. Schafer, *J. Am. Chem. Soc.,* 2011, **133**, 15453. (m) R. O. Ayinla, L. L. Schafer, *Dalton Trans.,* 2011, **40**, 7769. (n) E. Chong, S. Qayyum, L. L. Schafer, R. Kempe, *Organometallics,* 2013, **32**, 1858. (o) P. R. Payne, R. K. Thomson, D. M. Medeiros, G. Wan, L. L. Schafer, *Dalton Trans.,* 2013, **42**, 15670. (p) J. M. P. Lauzon, L. L. Schafer, *Z. Anorg. Allg. Chem.,* 2015, **641**, 128.

6 Selective reports on group 4 metal complexes catalyzed intermolecular hydroamination reactions: (a) P. J. Walsh, A. M. Baranger, R. G. Bergman, *J. Am. Chem. Soc.,* 1992, **114**, 1708. (b) E. Haak, I. Bytschkov, S. Doye, *Angew. Chem. Int. Ed.,* 1999, **38**, 3389. (c) J. S. Johnson, R. G. Bergman, *J. Am. Chem. Soc*., 2001, **123**, 2923. (d) F. Pohlki, S. Doye, *Angew. Chem. Int. Ed.,* 2001, **40**, 2305. (e) B. F. Straub, R. G. Bergman, *Angew. Chem. Int. Ed.,* 2001, **40**, 4632. (f) Y. Shi, J. T. Ciszewski, A. L. Odom, *Organometallics,* 2001, **20**, 3967. (g) C. Cao, J. T. Ciszewski, A. L. Odom, *Organometallics,* 2001, **20**, 5011. (h) A. Tillack, I. G. Castro, C. G. Hartung, M. Beller, *Angew. Chem. Int. Ed*., 2002, **41**, 2541. (i) A. Heutling, S. Doye, *J. Org. Chem.,* 2002, **67**, 1961. (j) V. Khedkar, A. Tillack, M. Beller, *Org. Lett.,* 2003, **5**, 4767. (k) C. Li, R. K. Thomson, B. Gillon, B. O. Patrick, L. L. Schafer, *Chem. Commun.,* 2003, 586. (l) Z. Zhang, L. L. Schafer, *Org. Lett*., 2003, **5**, 4733. (m) Y. Shi, C. Hall, J. T. Ciszewski, C. Cao, A. L. Odom, *Chem. Commun.,* 2003, 2462. (n) L. L. Anderson, J. Arnold, R. G. Bergman, *Org. Lett.*, 2004, **6**, 2519. (o) A. Tillack, V. Khedkar, M. Beller, *Tetrahedron Lett*., 2004, **45**, 8875. (p) A. Heutling, F. Pohlki, S. Doye, *Chem. Eur. J.,* 2004, **10**, 3059. (q) A. Tillack, H. Jiao, I. G. Castro, C. G. Hartung, M. Beller, *Chem. Eur. J.,* 2004, **10**, 2409. (r) A. Tillack, V. Khedkar, H. Jiao, M. Beller, *Eur. J. Org. Chem.,* 2005, 5001. (s) K. Marcseková, B. Wegener, S. Doye, *Eur. J. Org. Chem.,* 2005, 4843. (t) E. Chong, S. Qayyum, L. L. Schafer, R. Kempe, *Organometallics,* 2006, **25**, 6125. (u) A. V. Lee, L. L. Schafer, *Organometallics,* 2006, **25**, 5249. (v) Z. Zhang, D. C. Leitch, M. Lu, B. O. Patrick, L. L. Schafer, *Chem. Eur. J.,* 2007, **13**, 2012. (w) D. C. Leitch, P. R. Payne, C. R. Dunbar, L. L. Schafer, *J. Am. Chem. Soc*., 2009, **131**, 18246. (x) K. S. Weitershau, B. D. Ward, R. Kubiak, C. Müller, H. Wadepohl, S. Doye, L. H. Gade, *Dalton Trans.,* 2009, 4586. (y) D. C. Leitch, C. S. Turner, L. L. Schafer, *Angew. Chem. Int. Ed.,* 2010, **49**, 6382. (z) II, D. L. Swartz, R. J. Staples, A. L. Odom, *Dalton Trans.,* 2011, **40**, 7762. (aa) K. Born, S. Doye, *Eur. J. Org. Chem*., 2012, 764. (bb) I. A. Tonks, J. C. Meier, J. E. Bercaw, *Organometallics,* 2013, **32**, 3451. (cc) C. Brahms, P. Tholen,

W. Saak, S. Doye, *Eur. J. Org. Chem*., 2013, **33**, 7583. (dd) J. C. –H. Yim, J. A. Bexrud, R. O. Ayinla, D. C. Leitch, L. L. Schafer, *J. Org. Chem.,* 2014, **79**, 2015.

7 For recent reports: (a) E. Despagnet-Ayoub, M. K. Takase, J. A. Labinger, J. E. Bercaw, *J. Am*. *Chem. Soc*., 2015, DOI: 10.1021/jacs.5b06695. (b) A. C. Behrle, J. R. Levin, J. E. Kim, J. M. Drewett, C. L. Barnes, E. J. Schelter, J. R. Walensky, *Dalton Trans.,* 2015, **44**, 2693. (c) E. Bisz, M. Bialek, B. Zarychta, *Appl. Catal. A-Gen*., 2015, **503**, 26 (d) H. Schroeder, B. R. Lake, S. Demeshko, M. P. Shaver, M. Buback, *Macromolecules*, 2015, **48**, 4329. (e) F. Bonnet, H. E. Dyer, Y. El Kinani, C. Dietz, P. Roussel, M. Bria, M. Visseaux, P. Zinck, P. Mountford, *Dalton Trans.,* 2015, **44**, 12312. (f) J-B. Wang, L-P. Lu, J-Y. Liu, H-L. Mu, Y-S. Li, *J. Mol. Catal. A-Chem*., 2015, **398**, 289. (g) M. Tschage, S. Jung, T. P. Spaniol, J. Okuda, *Macromol. Rapid. Comm*. 2015, **36**, 219. (h) M. R. Radlauer, T. Agapie, *Organometallics,* 2014, **33**, 3247. (i) C. Hohberger, T. P. Spaniol, J. Okuda, *Macromol. Chem. Phys*. 2014, **205**, 2011. (j) S. Xiong, D. K. Steelman, G. A. Medvedev, W. N. Delgass, M. M. Abu-Omar, J. M. Caruthers, *ACS Catal.*, 2014, **4**, 1162. (k) L. Chiang, L. N. Allan, J. Alcantara, M. P. Wang, T. Storr, M. P. Shaver, *Dalton Trans.,* 2014, **43**, 4295. (l)T. Zeng, Q. Qian, B. Zhao, D. Yuan, Y. Yao, Q. Shen, *RSC Adv*., 2015, **5**, 53161. (m) T. R. Forder, M. D. Jones, *New. J. Chem*. 2015, **39**, 1974. (n) M. Zhang, X. Ni, Z. Shen, *Organometallics,* 2014, **33**, 6861. (o) Y. Chapurina, J. Klitzke, O. J. Casagrande, M. Awada, V. Dorcet, E. Kirillov, J-F Carpentier, *Dalton Trans.,* 2014, **43**, 14322. (p) K. Nie, T. Feng, F. Song, Y. Zhang, H. Sun, D. Yuan, Y. Yao, Q. Shen, *Sci. China. Chem.* 2014, **57**, 1106. (q) C. Romain, C. Fliedel, S. Bellemin-Laponnaz, S. Dagorne, *Organometallics,* 2014, **33**, 5730. (r) J. S. Klitzke, T. Roisnel, E, Kirillov, de L. Casagrande, J. Osvaldo, J-F. Carpentier, *Organometallics,* 2014, **33**, 309. (s) S. Yang, K. Nie, Y. Zhang, M. Xue, Y. Yao, Q. Shen, *Inorg. Chem*., 2014, **53**, 105. (t) M. Taherimehr, J. P. C. C. Serta, A. W. Kleij, C. J. Whiteoak, P. P. Pescarmona, *ChemSusChem*, 2015, **8**, 1034. (u)H. Chen, L. N. Dawe, C. M. Kozak, *Catal. Sci. Technol*., 2014, **4**, 1547. (v) T. Zeng, Y. Wang, Q. Shen, Y. Yao, Y. Luo, D, Cui, *Organometallics,* 2014, **33**, 6803. (w) W, Guerin, A. K. Diallo, E. Kirilov, M. Helou, M. Slawinski, J-M. Brusson, J-F. Carpentier, S. M. Guillaume, *Macromolecules*, 2014, **47**, 4230. (x) C. G. Jaffredo, Y. Chapurina, S. M. Guillaume, J. F. Carpentier, *Angew. Chem. Int. Ed*., 2014, **53**, 2687.

8 Q. Sun, Y. Wang, D. Yuan, Y. Yao, Q. Shen, *Organometallics,* 2014, **33**, 994.

9 Q. Sun, Y. Wang, D. Yuan, Y. Yao, Q. Shen, *Chem. Commun.,* 2015, **51**, 7633.

10 (a) E.Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt, *Organometallics,* 2001, **20**, 3017. (b) E.Y. Tshuva, I. Goldberg, M. Kol, H. Weitman, Z. Goldschmidt, *Chem. Commun.,* 2000, 379. (c) E.Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt, *Inorg. Chem. Commun.,* 2000, **3**, 611.

11 (a) E.Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt, *Inorg. Chem.,* 2001, **40**, 4263. (b) E.Y. Tshuva, M. Versano, I. Goldberg, M. Kol, H. Weitman, Z. Goldschmidt, *Inorg. Chem. Commun.,* 1999, **2**, 371.

12 Selected X-ray crystallographic data for zirconium complex **6**: Formula, $C_{44}H_{58}N_2O_4Zr$, C_7H_8; fw, 862.28; color, colorless; habit, prism; cryst size [mm], 0.60×0.50×0.40; temp [K], 223(2); crystsyst, monoclinic; space group, *P*2(1)/c; *a* [Å], 19.1566(9); *b* [Å], 16.0193(6); *c* [Å], 16.0089(7); β [deg], 110.2047(5)˚; *V*[Å^3], 4610.4(3); *Z*, 4; D_c [g cm^{-3}], 1.242; radiation used, Mo Kα; μ [mm^{-1}], 0.283; ϑ range, 2.85-26.37; no. of unique data, 4712; max, min transm, 1.000, 0.8600; final R indices [$I > 2\sigma(I)$], R_1 = 0.0395, wR_2 = 0.1094; *R* indices (all data), R_1 = 0.0470wR_2 = 0.1157; goodness-of-fit on F^2, 1.091; peak/hole [e Å^{-3}], 0.764/-0.623.

13 R. H. Platel, L. L. Schafer, *Chem. Commun.,* 2012, **48**, 10609.

14 (a) D. L. Swartz II, A. L. Odom, *Organometallics*, 2006, **25**, 6125. (b) F. Hild, S. Dagorne, *Organometallics*, 2012, **31**, 1189.

15 A. Lalitha, K. Pitchumani and C. Srinivasan, *Green Chemistry*, 1999, **1**, 173.

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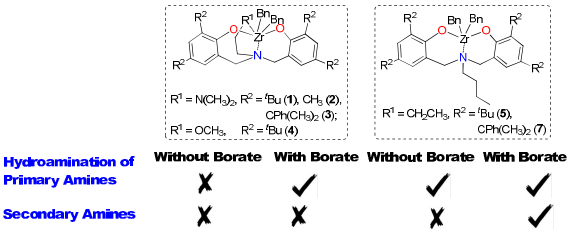

Pentacoordinate zirconium complexes **5** and **7** stabilized by amine-bridged bis(phenolato) ligands are more active than hexacoordinate complexes **1**-**4** in catalyzing intermolecular hydroamination reactions.