Group 4 Bis(pyrimidinoxide) Complexes. Investigations of Electronic Effects in Catalytic Hydroamination

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Substituted pyrimidinols, acidic aromatic alcohols, were used as proligands to synthesize metal complexes of Ti and Zr. These new pseudotetrahedral complexes were investigated as catalysts for the hydroamination of alkynes and alkenes. The stabilized anion of the pyrimidinoxide ligand results in enhanced electrophilicity at the metal center. These electronically modified complexes are catalytically active, but their enhanced reactivity results in reduced selectivity in comparison with the related bis(phenoxide) complexes in alkyne hydroamination. This reactivity was used to advantage in the cyclohydroamination of select aminoalkene substrates with the Zr bis(pyrimidinoxide) complex.

Introduction

Nitrogen-containing molecules are prevalent in nature and are found to have wide application in the pharmaceutical and agrochemical industries. More specifically, the imine and amine functionalities are useful synthetic building blocks,[1] are found in a number of natural products,[2] and are often used in detergents and dyes.[3] Given the importance of these types of molecules, much research has been devoted toward new methodologies for their syntheses, and most recently, the efficient preparation of imines and amines through hydroamination has been intensely investigated.[4] Many different substrates can be used for the hydroamination reaction, such that the C−C unsaturated bonds in alkynes, allenes, and alkenes can undergo reactions with primary amines, secondary amines, and hydrazines to yield a wide range of imine- and/or amine-containing products.

With few exceptions,[5] the hydroamination reaction requires the use of a catalyst. A number of catalyst systems with metals ranging across the periodic table have been designed for metal-mediated hydroamination, including late transition metals,[6] lanthanides,[7] actinides,[8] alkali and alkaline earth metals,[9] and early transition metals. However, no generalized catalyst system for this transformation has been developed. As early transition metals are relatively inexpensive and nontoxic, they are attractive for catalyst development. A number of research groups have been active in recent years in the synthesis of group 4 metal complexes for catalytic hydroamination, including the groups of Bergman,[10] Livinghouse,[11] Odom,[12] Beller,[13] Doye,[14] ourselves,[15] and others.[16]

Recent research efforts in group 4 hydroamination catalysis

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have demonstrated the importance of steric and electronic effects upon observed reactivity and regioselectivity.[12d,13a,b,16a,e] Our group has shown in a series of related bis(amidate) Ti complexes that the enhancement of the ionic bonding character between the auxiliary ligands and the reactive metal has resulted in the preparation of catalysts that display improved reactivity.[15a,b] Recently, the investigation of steric effects upon regioselectivity in Ti bis(phenoxide) complexes has been systematically probed, both experimentally and theoretically by Beller and co-workers.[13a,b,17] However, new compounds that contribute to a better understanding of the role of electronic properties in observed reactivity would further enhance our insight into ligand and catalyst design. To this end, we recently began using new proligands, substituted pyrimidinols such as **1**, as analogues to substituted phenols. Phenols have been extensively employed as proligands in group 4 organometallic chemistry,[18] and as mentioned above, the resultant titanium complexes have been investigated for regioselective alkyne hydroamination.[13a,b,17] While pyrimidinols are also aromatic alcohols, they display enhanced acidity in comparison with phenols and have a measured pK_a value of approximately 7.[19] Though the structural similarities and electronic differences between pyrimidinols and phenols have been exploited in physical organic investigations,[20] pyrimidinols remain unexplored as proligands in inorganic chemistry.

Here we report the synthesis and characterization of the first pyrimidinoxide complexes of titanium and zirconium. The structural and spectroscopic features of these isolable, crystalline materials are discussed. Most importantly, the enhanced reactivity that results because of the modified electronic properties of these complexes has been probed through catalytic investigations of alkyne and alkene hydroamination reactions.

Results and Discussion

Metal Complex Synthesis and Characterization. Previous work in the area of substituted phenoxide group 4 complexes noted that the use of phenol proligands lacking steric bulk in the 2- and 6-positions led to the formation of inactive titanium tris- and tetrakis(phenoxide)complexes.[13a,b,17] Furthermore, improved hydroamination catalytic activity was shown to be dependent upon bulk in the 2- and 6-positions on the phenoxide.[13a,b,17] With this in mind, we decided to investigate pyrimidinol **1** with *tert*-butyl in the ortho positions.

Proligand **1** is synthesized in three steps from commercially available 2,2,6,6-tetramethyl-3,5-heptanedione in 43% overall yield, using a literature procedure (Scheme 1).[20]

The corresponding bis(pyrimidinoxide)bis(amido)titanium-(IV) complex **2** is then synthesized via a protonolysis reaction between proligand **1** and tetrakis(dimethylamido)titanium (Scheme 1). This reaction proceeds very quickly at room temperature and is marked by a color change from light orange to deep orange-red. After removal of the volatile components, a dark orange solid is obtained that is soluble in all hydrocarbon solvents and is easily recrystallized from toluene. This complex displays excellent thermal stability and shows no detectable decomposition in solution at 110 °C over 10 days. Furthermore, this compound can be stored indefinitely at −35 °C under an inert atmosphere. The ^{1}H NMR spectrum of **2** shows a downfield shift in the *tert*-butyl signal from δ 1.36 in the proligand to δ 1.51, a smaller downfield shift for the *p*-methyl signal from δ 2.65 to δ 2.67, and the diagnostic disappearance of the OH

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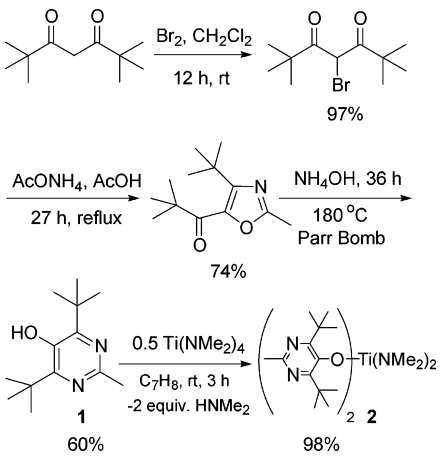
Scheme 1. Synthesis of the Substituted Pyrimidinol 1 and Its Ti Complex 2



signal at δ 4.31. There is no evidence in either the ^{1}H NMR or the ^{13}C NMR spectra of any nonvolatile byproducts being formed in this reaction. The ORTEP depiction of the solid-state molecular structure is shown in Figure 1, and selected bond lengths and angles are given in Table 1.

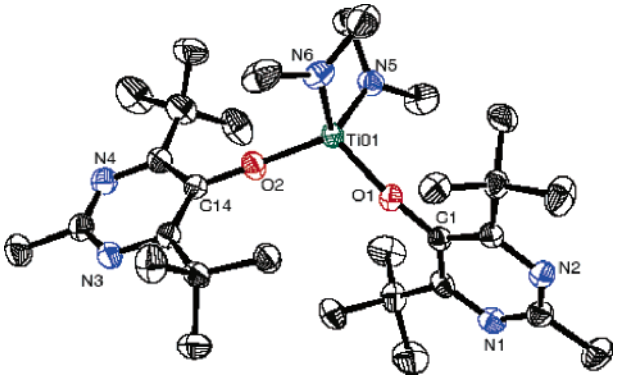


Figure 1. ORTEP depiction of **2**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are set to 50% probability.

The coordination geometry about the Ti atoms is a distorted tetrahedron, as expected, given the steric bulk of the pyrimidinoxide ligand and the literature precedence for analogous structurally characterized phenoxide complexes.[18a,b]

The Ti−O bond lengths in **2** are very similar in length (1.8408(13) and 1.8421(14) Å), which is in contrast to the case for **3** (Figure 2), where one of the Ti−O bonds was substantially longer than the other (1.860(3) versus 1.813(4) Å). Furthermore, the Ti−O bond lengths in **2** are longer than the shortest bond in **3** and both of the Ti−O bonds in **4** (1.808(2) and 1.828(2) Å). This is consistent with the electronic properties of the pyrimidinoxide ligand, which possesses bonding that is more ionic and less covalent in nature.[21] However, the observed bond length is still significantly shorter than the calculated Ti−O

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2

Ti−O(1)	1.8408(13)	Ti−N(6)	1.9065(17)
Ti−O(2)	1.8421(14)	O(1)−C(1)	1.351(2)
Ti−N(5)	1.8965(17)	O(2)−C(14)	1.356(2)
O(1)−Ti−N(5)	100.97(7)	Ti−O(1)−C(1)	172.17(13)
O(1)−Ti−N(6)	121.69(7)	Ti−N(5)−C(29)	123.92(14)
O(2)−Ti−N(5)	121.91(7)	Ti−N(5)−C(30)	125.29(15)
O(2)−Ti−N(6)	101.89(7)	C(29)−N(5)−C(30)	110.75(18)
O(1)−Ti−O(2)	112.36(7)	Ti−N(6)−C(27)	123.07(16)
N(5)−Ti−N(6)	98.70(8)	Ti−N(6)−C(28)	126.28(16)
Ti−O(2)−C(14)	176.76(14)	C(27)−N(6)−C(28)	110.6(2)

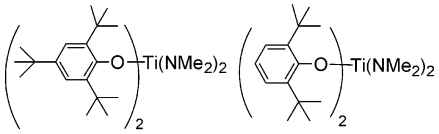


Figure 2. Related fully characterized bis(phenoxide)bis(amido)-titanium complexes.

single covalent bond length of 2.01 Å and indicates a degree of π-bonding. The Ti−O−C bond angles of 176.76(14) and 172.17(13)° also support multiple-bond character, and these angles resemble the bond angles reported for **4** (these angles are similar to one angle reported for **3** but not to the other, given the difference in the bonding of the two phenoxide ligands in that molecule).

The lengths of the Ti−N bonds are both shorter than a Ti−N single bond (1.96 Å), and the sum of the angles about N5 and N6 indicate that the nitrogen atoms are planar. These observations indicate some π bonding, as has been observed for both **3** and **4**.

The bis(pyrimidinoxide)bis(amido)zirconium complex **5** can also be synthesized by an analogous protonolysis reaction with tetrakis(dimethylamido)zirconium as the commercially available metal starting material. Complex **5** is cleanly formed in 96% yield and isolated as a stable white solid that can also be stored indefinitely at −35 °C under an inert atmosphere. The ^{1}H NMR spectrum shows a shift in the *tert*-butyl resonances from δ 1.36 to δ 1.50. The *p*-methyl resonance also shifted from δ 2.65 to δ 2.67, and again the O−H peak at δ 4.31 disappeared. The successful synthesis of **5** is further supported by ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis.

It was hoped that the use of these bulky, highly acidic proligands would lead to Ti and Zr complexes which exhibit resistance to hydrolysis greater than that normally attributed to group 4 metal complexes. In particular, Beller and co-workers reported that the bulky bis(phenoxide)bis(amido)titanium complexes could be handled for short amounts of time in air without loss of reactivity. The development of new catalysts that may be used without any specialized handling techniques is attractive for their application in complex organic synthesis. Indeed, both **2** and **5** can be handled in the open laboratory for short periods (minutes) without consequence. However, long-term exposure to atmospheric moisture results in their obvious decomposition, with one crystalline example of a decomposition product of complex **5**, the oxo-bridged species **6**, being presented in Figure 3; selected bond lengths and angles are given in Table 2. This product retains both of the bis(pyrimidinoxide) ligands and one of the amido ligands on each Zr metal center. In the solid state, the remaining amido ligands are eclipsed and have π-bonding character, as evidenced by the planar, sp^2 hybridization of N. The Zr−O bonds of the pyrimidinoxide ligands are typical,[22] and the Zr−O−Zr bond angle of 164.1(3)° is intermediate for previously reported Zr μ-O species (range 142° to 180°).[23]

Applications in Hydroamination Catalysis. With complexes **2** and **5** in hand, we investigated their reactivity trends in catalytic hydroamination. This investigation focused on both relative catalytic activity as well as regioselectivity in the

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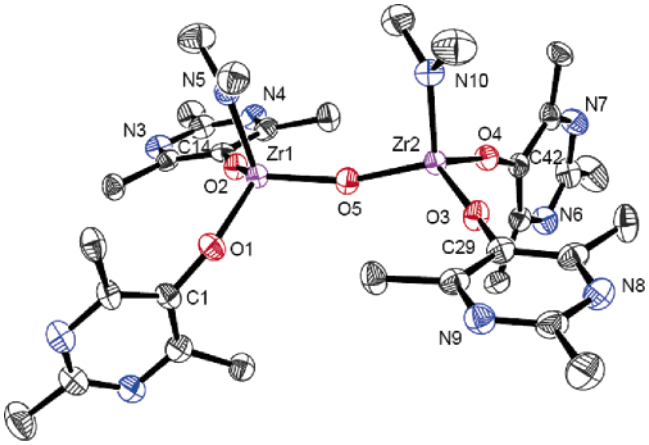
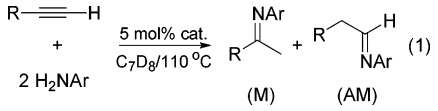


Figure 3. ORTEP plot of **6**, a decomposition product of **5**. The methyls of the *tert*-butyl substituents and the hydrogen atoms have been omitted for clarity. Thermal ellipsoids are set to 50% probability. The SQUEEZE procedure was used to take care of the contribution of disordered hexanes within the crystal lattice.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 6

Zr(1)−O(5)	1.956(5)	Zr(1)−N(5)	2.009(7)
Zr(2)−O(5)	1.960(6)	Zr(2)−N(10)	2.001(7)
Zr(1)−O(1)	1.961(6)	O(1)−C(1)	1.361(10)
Zr(1)−O(2)	1.938(5)	O(2)−C(14)	1.366(10)
Zr(2)−O(3)	1.959(5)	O(3)−C(29)	1.350(10)
Zr(2)−O(4)	1.965(5)	O(4)−C(42)	1.345(10)
Zr(1)−O(5)−Zr(2)	164.1(3)	O(4)−Zr(2)−N(10)	109.8(3)
O(1)−Zr(1)−O(2)	113.3(2)	O(1)−Zr(1)−O(5)	107.8(2)
O(3)−Zr(2)−O(4)	113.5(2)	O(2)−Zr(1)−O(5)	119.6(2)
O(1)−Zr(1)−N(5)	108.8(3)	O(3)−Zr(2)−O(5)	119.1(2)
O(2)−Zr(1)−N(5)	101.9(3)	O(4)−Zr(2)−O(5)	107.9(2)
O(3)−Zr(2)−N(10)	101.7(3)		

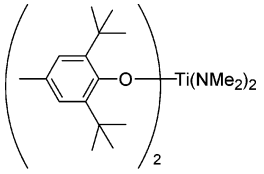
Table 3. Hydroamination Results with Arylamines



entry	R	Ar	cat.	time (h)	yield (%)[a]	M:AM[a]
1	Ph	Ph	**2**	16	52	7:3
2	Ph	Ph	**5**	16	44	>20:1
3	Ph	Ph	**5**	64	71	>20:1
4	Bn	Ph	**2**	16	67	7:3
5	Bn	Ph	**5**	16	22	>20:1
6	Bn	Ph	**5**	64	48	>20:1
7	^{n}Bu	Ph	**2**	16	72	4:1
8	^{n}Bu	Ph	**5**	16	11	>20:1
9	^{n}Bu	Ph	**5**	64	52	>20:1
10	Ph	Ar*[b]	**2**	16	78	3:2
11	Bn	Ar*	**2**	16	78	>20:1

[a] Determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. [b] Ar* = 2,6-dimethylphenyl.

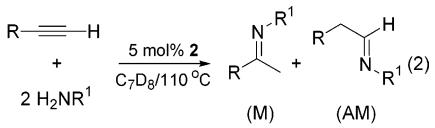
reaction between terminal alkynes and primary arylamines (eq 1, Table 3). In all cases with **2** as the precatalyst, the reaction goes to complete conversion within 16 h, as evidenced by the disappearance of alkyne. With **5** as the precatalyst, on the other hand, the reaction never goes to complete conversion, even with reaction times of up to 64 h, at which point the reactions were discontinued. Furthermore, **2** is able to perform hydroamination with both aniline and 2,6-dimethylaniline, whereas **5** shows no reaction with 2,6-dimethylaniline. With both catalyst systems, the Markovnikov product is the predominant product. It is also interesting to note that while **2** led to complete conversion of the starting material (terminal alkyne), the yields of the reactions are much lower (52−78%). This could be due to side reactions



7

Figure 4. Bis(phenoxide)bis(amido)titanium catalyst investigated by Beller and co-workers.

Table 4. Hydroamination of Terminal Alkynes with Alkylamines Using 2 as a Precatalyst



entry	R	R^1	yield (%)[a]	M:AM[a]
1	Ph	^{t}Bu	82	1:2
2	Ph	^{i}Pr	83	2:3
3	Ph	Bn	61	3:2
4	Bn	^{t}Bu	>95	1:4
5	Bn	^{i}Pr	>95	2:3
6	Bn	Bn	82	1:1
7	^{n}Bu	Bn	80 (62)[b]	3:2

[a] Determined by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard. [b] Isolated yield after reduction with $NaBH_3CN$/$ZnCl_2$ and column chromatography.

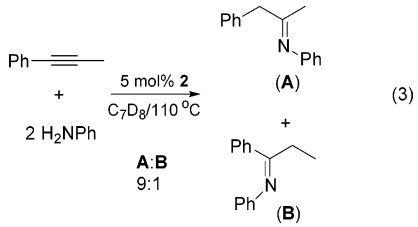
resulting from uncontrolled reactivity, such as alkyne oligomerization.[17a] Furthermore, in entries 1−3 there is evidence of enamine formation in the ^{1}H NMR spectra, which is not accounted for in the reported yield of the reaction.[17b]

Beller and co-workers have investigated a number of substituted phenols as proligands for titanium-catalyzed hydroamination, and **7** (Figure 4) was shown to be active in the hydroamination of terminal alkynes with primary amines.[13a] As was the case with **2** and **5**, when aniline was used as the primary amine, **7** was reported to form predominantly the Markovnikov product.

These initial investigations with arylamines show that the titanium complex is a better catalyst than the zirconium analogue. This has been observed before in the hydroamination of alkynes.[15a] Furthermore, precatalyst **5** fails to catalyze any hydroamination reaction when using alkylamines. Precatalyst **2**, on the other hand, does promote the hydroamination between terminal alkynes and primary alkylamines, and the results are summarized in Table 4. In general, there is less regioselectivity observed with alkylamines than with arylamines. Again, it is noted that in all cases the reaction goes to complete conversion, though the yields are more moderate. The yields are an improvement, however, over what is observed with the arylamines. One possible reason for this observation is that there is greater reactivity with arylamines, as the reactions will proceed, albeit more slowly, at 65 °C, whereas hydroamination with alkylamines requires elevated temperatures. This lower temperature observed for satisfactory reactivity suggests that greater uncontrolled reactivity is occurring with arylamines, resulting in lower yields of the desired products. An increase in regioselectivity for the anti-Markovnikov imine is observed when using the bulky ^{t}Bu amine (entries 1 and 4), and this regioselectivity decreases as the steric bulk of the amine decreases. With the use of benzylamine (entries 3, 6, and 7) the Markovnikov product is favored, though the regioselectivity is not high. When these reactions were performed with pre-

catalyst **7**, Beller and co-workers reported a high regioselectivity for the Markovnikov product with alkylamines other than *tert*-butylamine, including benzylamine.[13b] In the phenoxide case, when using *tert*-butylamine, a lower conversion (only 50% when there are two ligands on the Ti) was observed, along with regioselectivity for the anti-Markovnikov amine.[17a] These direct comparisons of reactivity demonstrate the higher, but less controlled, reactivity observed for the pyrimidinoxide complexes.

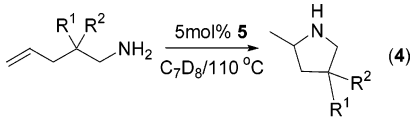
After investigating the intermolecular hydroamination of terminal alkynes with aryl and alkylamines, we then turned our attention to the hydroamination reaction of internal alkynes. The reaction between the unsymmetrical 1-phenyl-1-propyne and aniline with complex **2** yields two isomeric products (eq 3) in



(3)

71% combined yield, as determined by ^{1}H NMR spectroscopy after 40 h, with **A** being the preferred product. The analogous reaction with 2,6-dimethylaniline gives only compound **A** in 31% yield after 40 h. The reaction between 1-phenyl-1-propyne and alkylamines is not clean and does not go to complete conversion, even after 40 h at 110 °C. The hydroamination of symmetrical internal alkynes such as 3-hexyne and diphenylacetylene in modest yield (up to 50%) after 120 h with aniline at 110 °C, and does not occur at all with alkylamine substrates. Again, precatalyst **5** is unable to catalyze these reactions.

The difference in pK_a values between the pyrimidinol proligand and a phenol proligand is over 3 (pyrminidinol pK_a = 6.8 and phenol pK_a = 9.9).[20] As is observed with the investigations into the hydroamination of terminal alkynes, this change in electronic properties leads to an apparent increase in uncontrolled reactivity, as marked by the high conversions but moderate yields. This increase in reactivity also results in a decrease in regioselectivity for the reaction with terminal and internal alkynes. However, enhanced reactivity suggests that this class of complexes be evaluated for the more challenging intramolecular hydroamination of aminoalkenes (eq 4).



(4)

R^1=Ph R^2=Ph >95% yield after 64h
R^1=Ph R^2=Me 73% yield after 150h

When using precatalyst **2**, no reactivity is observed for the above reaction. However, the move to precatalyst **5**, which is less active in the hydroamination of terminal alkynes, does lead to the slow formation of amine product. The observation that the Zr congener is more reactive than the Ti version in the cyclohydroamination of aminoalkenes has been previously noted.[24] When $R^1 = R^2$ = Ph, the gem-disubstituent effect, incorporating both the Thorpe−Ingold effect and the reactive-rotamer effect, can assist the hydroamination reaction, and as this effect decreases with decreasing size (eg. R^1 = Ph, R^2 = Me), the reactivity of the system also decreases, as evidenced by the lower yield and longer reaction time. Finally, no reaction is observed when both R^1 and R^2 are methyl groups. This is in contrast to recently reported efficient systems that perform the aforementioned cyclization in high yield.[25]

Table 5. Details of the X-ray Structure Determinations of 2 and 6

	2	**6**
empirical formula	$C_{30}H_{54}N_6O_2Ti$	$C_{56}H_{96}N_{10}O_5Zr_2$
fw	578.69	1171.87
cryst color, habit	orange, prism	colorless, needle
cryst size (mm)	0.5 × 0.5 × 0.3	0.2 × 0.2 × 0.15
cryst syst	orthorhombic	monoclinic
space group	$Pc2_1n$	$P2_1/n$
a (Å)	10.5710(8)	15.3557(9)
b (Å)	17.7226(14)	17.0718(10)
c (Å)	17.9379(15)	27.0530(13)
α (deg)	90	90
β (deg)	90	90.235(2)
γ (deg)	90	90
V (Å^3)	3360.6(5)	7091.9(7)
Z	4	4
D_{calcd} (Mg/m^3)	1.144	1.098
F(000)	1256	2488
μ(Mo Kα) (cm^{-1})	0.288	0.339
λ(Mo Kα) (Å)	0.710 80	0.710 73
temp (K)	173	173
θ range (deg)	2.24−27.81	2.331−20.493
$2\theta_{max}$ (deg)	55.62	40.986
no. of rflns measd		
total	69 514	97 415
unique	7886	9924
R(int)	0.0488	0.0928
structure soln	Sir92	Sir92
max, min transmissn	0.917 227, 0.001 375 84	1.00, 0.8314
no. of variables	380	658
rfln/param ratio	20.7526	15.0821
residuals: R, R_w	0.0518, 0.1057	0.1038, 0.2791
goodness of fit	1.024	1.134
max, min peaks final diff map (e/Å3)	0.413, −0.176	3.756, −0.522

Summary and Conclusions

The use of substituted pyrimidinols as proligands led to the synthesis of new, robust group 4 metal complexes that resemble known phenoxide complexes of Ti. These complexes possess a higher degree of ionic bonding than their phenoxide counterparts. The effects of this change in electronic structure of the metal complex for the intermolecular hydroamination of terminal alkynes was seen, as there was an observed increase in general reactivity and a concomitant decrease in selectivity, resulting in more byproducts, reduced product yields, and reduced regioselectivity. These results show that pyrimidinoxide ligands can be used as strongly anionic versions of phenoxide ligands to enhance reactivity at electropositive metal centers. This enhanced reactivity was advantageous, establishing a bis(pyrimidinoxide)bis(amido)zirconium complex as a competent catalyst for the hydroamination of select aminoalkenes.

Experimental Section

General Considerations. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker 300 or 400 MHz Avance spectrometer at room temperature, and chemical shifts are given relative to residual solvent. MS (ESI), MS (EI), elemental analysis, and single-crystal X-ray structure determinations were performed at the Department of Chemistry, University of British Columbia. Details

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of these determinations are given in Table 5. Synthesis of the metal complexes and assembly of the hydroamination reactions were done under the inert atmosphere of a nitrogen glovebox. Organic reagents were purchased from Aldrich and used without further purification for the ligand synthesis. $Ti(NMe_2)_4$ and $Zr(NMe_2)_4$ was purchased from Strem or Aldrich and used as received. Toluene and hexanes were purified on an Alumina column before use. d_8-Toluene was degassed and dried over molecular sieves. Phenylacetylene and 1-hexyne was purchased from Aldrich, dried over molecular sieves for 24 h, distilled, and degassed before use. 3-Phenylpropyne was synthesized via a literature procedure[26] and degassed before use. All primary amines were dried over CaH_2 for 24 h, distilled, degassed, and stored over molecular sieves. The aminoalkenes 2,2-diphenyl-4-pentenylamine[7e] and 2-methyl-2-phenyl-4-pentenylamine[27] were prepared using modified literature procedures.

Synthesis of the Ti Complex. In a small vial 0.41 g (1.85 mmol) of **1** was dissolved in 1 mL of toluene inside the glovebox before being added dropwise to a stirred solution of 0.21 g (0.92 mmol) of $Ti(NMe_2)_4$ in 1 mL of toluene in a 25 mL Teflon-capped vial at room temperature. The dark red solution was stirred at room temperature for 3 h before the solvent was removed; the residue was redissolved in hexanes, and this solution was filtered through Celite and concentrated to give a dark orange powder of **2** in 98% yield. X-ray-quality crystals could be obtained from recrystallization from toluene. ^{1}H NMR (300 MHz, d_8-toluene): δ 1.51 (36H, s, ^{t}Bu), 2.67 (6H, s, CH_3), 3.05 (12H, s, N−CH_3). ^{13}C NMR (100 MHz, d_8-toluene): δ 25.5, 29.9, 38.7, 47.8, 155.6, 156.6, 163.8. EI MS: m/z 578 (M^+), 535 (M − NMe_2). Anal. Calcd for $C_{30}H_{54}N_6O_2Ti$: C, 62.27; N, 14.52; H, 9.41. Found: C, 61.96; N, 14.33; H, 9.48.

Synthesis of the Zr Complex. In a small vial 0.3 g (1.35 mmol) of **1** was dissolved in 1 mL of toluene inside the glovebox before being added dropwise to a stirred solution of 0.18 g (0.67 mmol) of $Zr(NMe_2)_4$ in 1 mL of toluene in a 25 mL Teflon-capped vial at room temperature. The solution was stirred for 3 h before the solvent was removed; the residue was redissolved in hexanes, and this solution was filtered through Celite and concentrated to give **5** as a white powder in 96% yield. ^{1}H NMR (300 MHz, d_8-toluene): δ 1.50 (36H, s, ^{t}Bu), 2.67 (6H, s, CH_3), 2.89 (12H, s, N−CH_3). ^{13}C NMR (100 MHz, d_8-toluene): δ 25.5, 29.9, 38.3, 43.2, 152.1, 156.7, 163.4. EI MS: m/z 622 (M^+), 577 (M − NMe_2), 534 (M − 2NMe_2). Anal. Calcd for $C_{30}H_{54}N_6O_2Zr$: C, 57.93; N, 13.51; H, 8.75. Found: C, 57.56; N, 13.16; H, 8.73.

General Procedure for the Alkyne Hydroamination Reaction. In a small vial 0.004 g (0.007 mmol) of catalyst (**2** or **5**) was combined with 0.023 g (0.14 mmol) of 1,3,5-trimethoxybenzene, 0.14 mmol of alkyne, 0.28 mmol of primary amine, and 1 mL of d_8-toluene before being transferred to a sealable J. Young tube. The solution was heated at 110 °C for the indicated period of time. Conversions were calculated by the disappearance of the alkyne methine signal, and yields were calculated using a well-defined product signal. Only the imine contribution was included in the yield calculation, though in a few cases (namely with phenylacetylene) there was also enamine present, leading to an underestimation of the reported yield.

General Procedure for the Aminoalkene Hydroamination Reaction. In a small vial 0.14 mmol of aminoalkene was combined with 0.004 g (0.007 mmol) of **5** and 0.023 g (0.14 mmol) of 1,3,5-trimethoxybenzene in 1 mL of d_8-toluene in a sealed J. Young tube. The solution was heated at 110 °C for the indicated period of time. Conversions were calculated by the disappearance of the alkene signals, and yields were calculated using a well-defined product signal.

Acknowledgment. We thank Robert K. Thomson for assistance with X-ray crystallography and the UBC and NSERC for funding. A.V.L. thanks the NSERC for a graduate fellowship.

Supporting Information Available: Tables giving details on crystallographic studies for **2** and **6**, CIF files giving X-ray crystallographic data for **2** and **6**, and representative NMR spectra for the determination of yields in hydroamination reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060587B

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