Intramolecular Hydroaminations of Aminoalkynes Catalyzed by Yttrium Complexes and Aminoallenes Catalyzed by Zirconium Complexes

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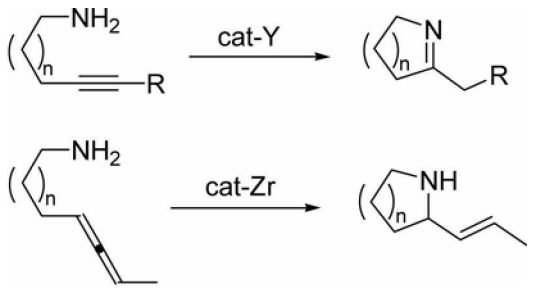
It was demonstrated that $Y[N(TMS)_2]_3$, the neutral yttrium-diamine complex **13** and yttrium-NPS complexes **15** are efficient precatalysts for intramolecular hydroamination of aminoalkynes involving primary amines. Complex **13** and **15** were quantitatively prepared *in situ* by direct metalation of the ligands **4** and **9** with 1 equiv of $Y[N(TMS)_2]_3$ in benzene-d_6 at 120 °C for 5 days and 10 days, respectively, *via* elimination of $(TMS)_2NH$. 5-*Exo*- and 6-*exo-dig* intramolecular hydroamination of aminoalkynes using catalyst **12** and **13** proceeded smoothly to give nitrogen-contained cyclic products in good to excellent yields in all cases. In the case of 7-*exo-dig* intramolecular hydroamination, the desired product was produced in 41% and 48% yields despite the *gem*-dimethyl effect. However, treatment of catalyst **15** with aminoalkynes (**19** and **22**) having a methyl substituent at the carbon adjacent to triple bond and 6-*exo-dig* intramolecular hydroamination of **21** failed to give the desired products. Zirconium-catalyzed intramolecular hydroamination of aminoallenes (**25**, **27**, and **31**) with 5 mol% **16** afforded 2-(*trans*-1-propenyl)pyrrolidine, 2-isopropylenepyrrolidine, and 2-(*trans*-1-propenyl)piperidine in 96%, 95%, and 93% yield, respectively. However, subjecting **25** to 5 mol% **15** was unsuccessful to produce the desired product.

Key Words : Intramolecular hydroamination, Aminoalkyne, Aminoallene, Yttrium, Zirconium

Introduction

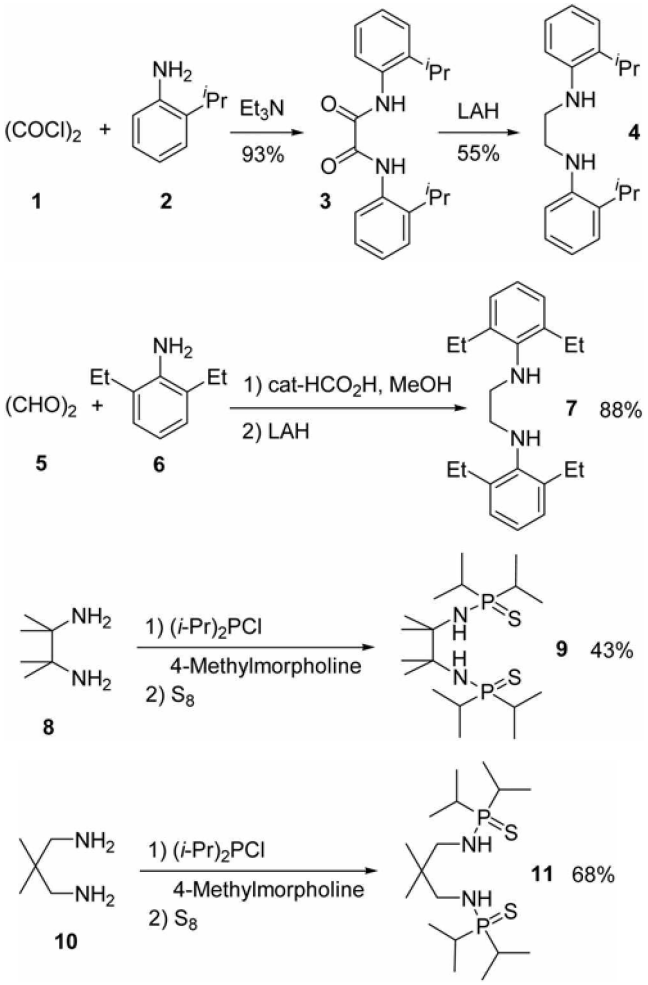
Transition metal-catalyzed intramolecular hydroamination of aminoalkynes and aminoallenes has been regarded as a powerful method for the synthesis of nitrogen-contained heterocyclic compounds.[1] Early metal-based catalysts for this conversion are well-suited for hydroaminations of aminoalkenes and aminoalkynes under mild reaction conditions. Various complexes that have been historically used for this purpose are relatively air- and moisture-sensitive metallocene derivatives.[2] Recently, organolanthanide-catalyzed processes have been expanded beyond the ability to form C-C bonds. Also, these organometallics are recognized to produce new C-N bonds efficiently by insertion of alkenes and alkynes into the metal-nitrogen bond of organolanthanide amides.[3] Effective non-metallocene lanthanide as well as group 3 catalysts were recently described for hydroamination reaction of aminoalkenes and aminoalkynes.[4] We found that simple amido derivatives of the group 3 metals corresponding to the formula $Ln[N(TMS)_2]_3$ (Ln = lanthanide, TMS = trimethylsilyl) and $[L_2YN(TMS)_2$ (L=ligand)] are efficient catalysts for intramolecular hydroamination of aminoalkenes and aminoalkynes and that zirconium(IV) complexes are fruitful catalyst for internal alkene hydroaminations.[5] Herein, $L_2YN(TMS)_2$ obtained from coordination of the active metal center to simple chelating diamide ligands could be effectively applied to intramolecular hydroamination of aminoalkynes and the neutral zirconium(IV) complex derived from $Zr(NMe_2)_4$ and NPS ligand has been shown to be an effective precatalyst for intramolecular hydroamination of aminoallenes, producing the cyclic amines in good to excellent yields (Scheme 1).[6]



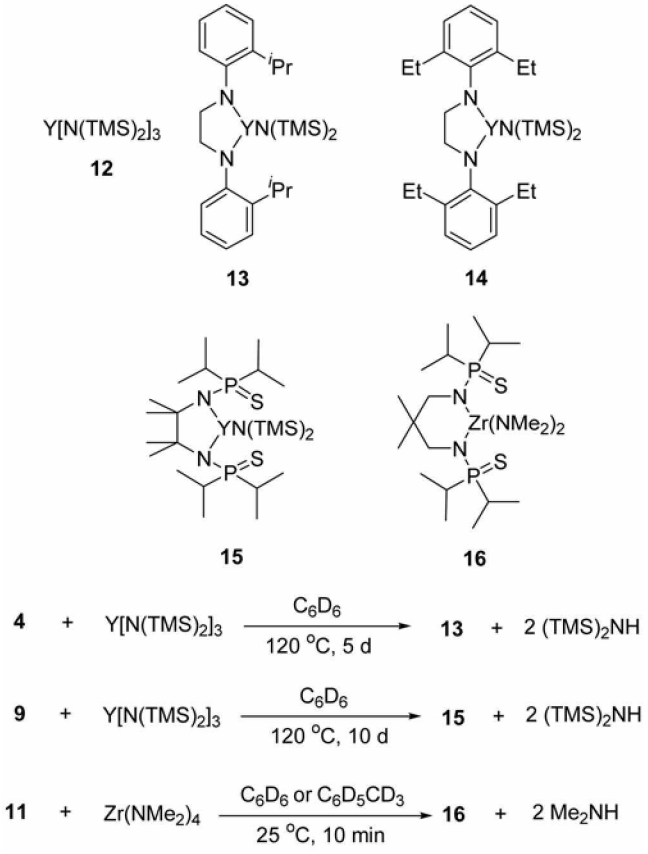
Scheme 1. Inromolecular hydroamination of aminoalkynes and aminoallenes.

Results and Discussion

Preparation of Ligand, Precatalyst, Aminoalkynes, and Aminoallenes: 1,2-Diamine proligand (**4**) was prepared by the reaction of 2-isopropylaniline (**2**) with oxalyl chloride (**1**) in the presence of triethylamine followed by reduction with LAH (Scheme 2). Treatment of 2,6-diethylaniline (**6**) with glyoxal (**5**) in the presence of catalytic amounts of formic acid in methanol gave 1,2-diimine compounds followed by reduction with LAH to afford the desired product (**7**) in 88% yield. The thiophosphinic amides (**9** and **11**) were prepared in 43% and 68% yields, respectively, by the reaction of 2,3-dimethyl-2,3-butanediamine (**8**) and 2,2-dimethyl-1,3-diamine (**10**) with 2.1 equiv of diisopropyl-



Scheme 2. Preparation of 1,2-diamines and NPS ligands.

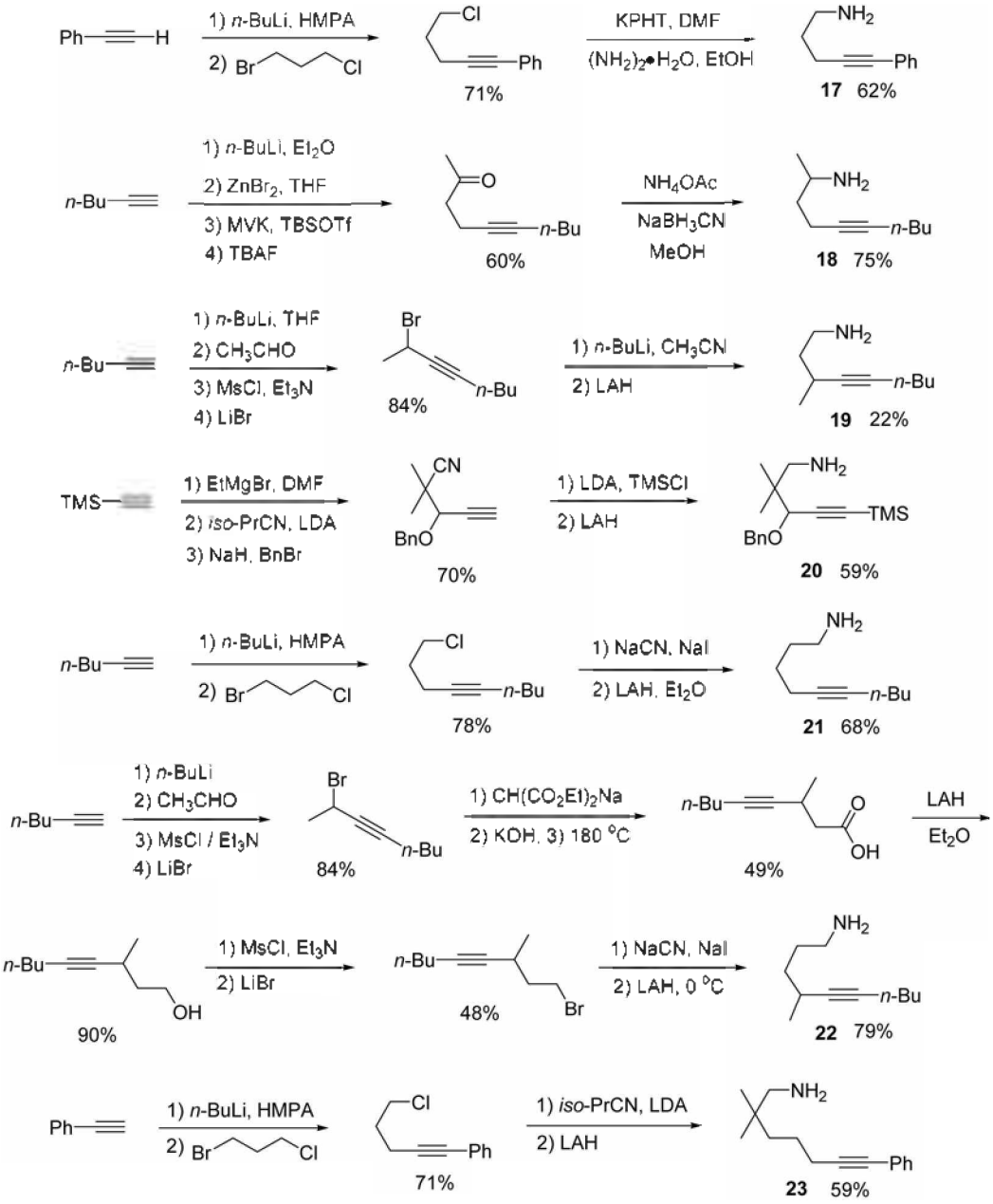


Scheme 3. In situ generation of yttrium and zirconium precatalyst for hydroamination.

chlorophosphine followed by the addition of 2.2 equiv of sulfur.

As part of our previous study,[5a] we noted that treatment of a variety of aminoalkenes with catalytic amounts of $Y[N(TMS)_2]_3$ (**12**) in benzene-d_6 at 24 °C resulted in generation of the corresponding amine-ligated amido complexes[7] accompanying the instantaneous liberation of $(TMS)_2NH$. It is well established that the catalytic activity of group 3 metallocenes in hydroamination of aminoalkynes is effected by steric hindrance about the metal center.[3] In the light of this, we began to examine the role that sterically hindered chelating diamide ligands might play in changing the reactivity of group 3 and 4 amido complexes (Scheme 3). Although metallation reaction of *N,N'*-bis(2,6-diethylphenyl)ethylenediamine (**7**) to yttrium was not completed even after 5 days, attachment of the ligand **4** to yttrium was quantitatively achieved by the direct metalation with 1 equiv of $Y[N(TMS)_2]_3$ in benzene-d_6 (120 °C, 5 days) to afford complex **13** *via* extrusion of $(TMS)_2NH$. Ligand exchange reaction of *N,N'*-bis(*P,P*-diisopropylthiophosphinyl)-2,3-dimethyl-2,3-butanediamine (**9**) with $Y[N(TMS)_2]_3$ proceeded to produce precatalyst **15** in benzene-d_6 (120 °C, 10 days) *via* elimination of bis(trimethylsilyl)amine. Also, attachment of the proligand **11** to zirconium was quantitatively attained by the direct metalation with 1 equiv of $Zr(NMe_2)_4$ in benzene-d_6 or toluene-d_8 (25 °C, 10 min) to give complex **16** [NPS·$Zr(NMe_2)_2$] *via* dimethylamine liberation. The ^1H, ^{13}C, and ^{31}P NMR spectra of **16** are consistent with a monomeric species possessing an octahedral structure in which both dimethylamino ligands are axial. The NMe_2 resonance (500 MHz) appears as a sharp singlet at 3.11 ppm and the linker CH_2 as a doublet (2.69 ppm, J = 10 Hz). The signal for the CH adjacent to phosphorus appears as a well defined septet centered at 2.00 ppm (J = 7 Hz), with the diastereomeric isopropyl methyls appearing as a set of doublets between 1.16 and 1.10 ppm (J = 7 Hz). The ^{31}P spectrum of **16** reveals a singlet at 75.10 ppm.[8] The thermal stability of **16** was described by heating it at 150 °C for 19 h, whereupon no alteration of the NMR spectra was detected.

Synthetic procedures for the synthesis of a variety of aminoalkynes are shown in Scheme 4. 5-Phenyl-4-pentyn-1-amine (**17**) was prepared by the reaction of phenylacetylene with 3-bromo-1-chloropropane using *n*-BuLi followed by a Gabriel reaction. 2-Amino-5-decyne (**18**) was obtained from the 1,4-addition of 1-hexyne to methyl vinyl ketone and reductive amination. The reaction of 2-bromo-3-octyne, derived from 1-hexyne and acetaldehyde, with lithiated acetonitrile followed by LAH reduction of nitrile produced 1-amino-3-methyl-4-nonyne (**19**). Also, preparations of **20**

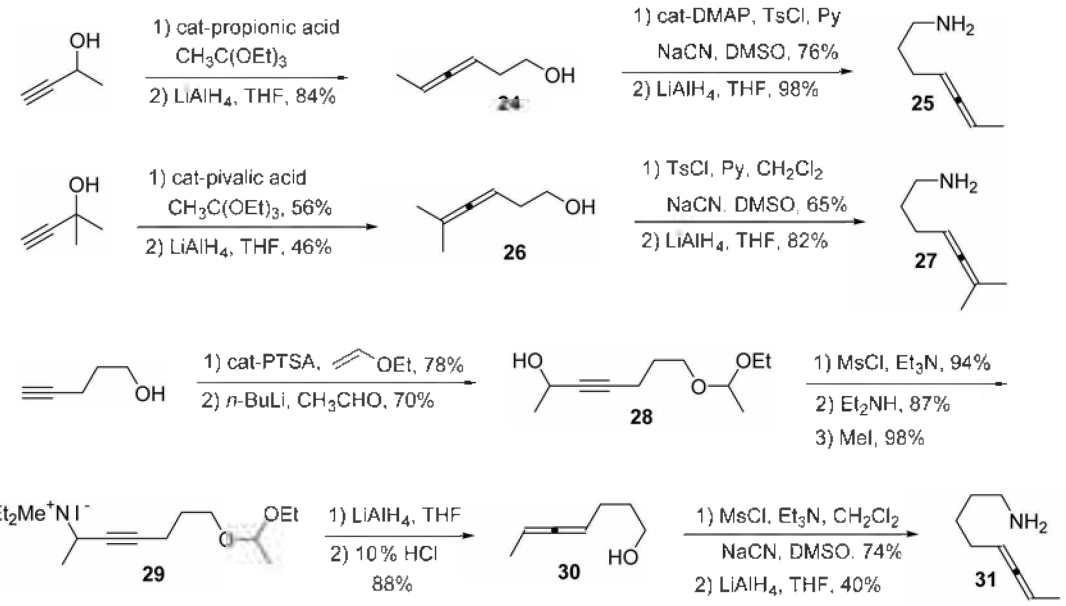


Scheme 4. Preparation of a variety of aminoalkynes.

and **22** could be achieved by using standard organic reactions. 1-Amino-5-decyne (**21**) and 1-amino-2.2-dimethyl-7-phenyl-6-heptyne (**23**) were prepared by alkylation of the correspondding acetylene and substitution by cyanide anion followed by reduction of nitrile with LAH.

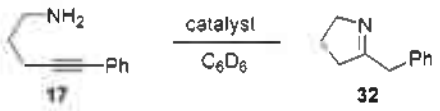
4.5-Heptadien-1-amine (**25**), 6-methyl-4.5-heptadien-1-amine (**27**), and 5.6-octadien-1-amine (**31**) were prepared from 3-butyn-2-ol, 2-methyl-3-butyn-2-ol, and 4-pentyn-1-ol, respectively (Scheme 5). 3.4-Hexadien-1-ol (**24**) was produced from the reaction of 3-butyn-2-ol with triethyl orthoacetate in the presence of catalytic amount of propionic acid followed by LAH reduction. Sulfonation of **24** with tosyl chloride, substitution of tosylate with sodium cyanide and then, LAH reduction gave rise to **25**. Also, compound **27** was similarly prepared to **25**. Compound **31** was easily obtained from standard organic reactions.

Yttrium-catalyzed Intramolecular Hydroamination of Aminoalkynes: First, the intramolecular hydroamination of 5-phenyl-4-pentyn-1-amine (**17**) was selected for initial examination of the catalytic activity of the complexes **12**, **13**, and **15**. The results are summarized in Table 1. Reaction of **17** with 5 mol% Y[N(TMS)$_2$]$_3$ (**12**) and **13** gave rise to the desired product 3,4-dyhydro-5-(phenylmethyl)-2*H*-pyrrole (**32**) in 90% (25 °C, 480 h) and 67% (25 °C, 330 h) yields, respectively, *via* 5-*exo*-*dig* intramolecular hydroamination (entries 1 and 3) in J. Young NMR tube (benzene-d_6, 0.46 M).[9] Heating the reaction mixture at 60 °C with 5 mol% Y[N(TMS)$_2$]$_3$ proceeded more rapidly to afford **32** in 90% yield after 89 h (entry 2). Exposure of **13** (5 mol%) to **17** produced azacycles in 94% yield (60 °C, 9 h, 1.0 M, entry 5).



Scheme 5. Preparation of 4,5-heptadine-1-amine, 6-methyl-4,5-heptadien-1-amine, and 5,6-octadien-1-amine.

Table 1. Reaction optimization of yttrium-catalyzed intramolecular hydroamination of 5-phenyl-4-pentyn-1-amine[a]



Entry	Catalyst	Conc. [M]	Temp. [°C]	Time [h]	Yield [%][b]
1	**12**	0.46	25	480	90
2	**12**	0.46	60	89	90
3	**13**	0.46	25	330	67
4	**12**	1.0	60	80	96
5	**13**	1.0	60	9	94(85)[c]
6	**15**	1.0	60	1.5	96

[a]Reaction performed in the presence of 5 mol % catalyst in benzene-d_6. [b]NMR yields based on *p*-xylene as an internal standard. [c]Isolated yield.

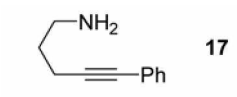
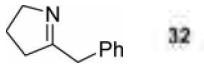
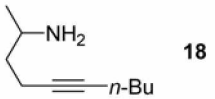
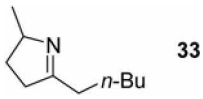
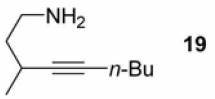
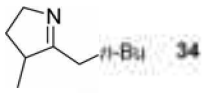
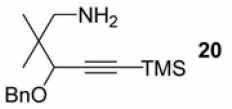
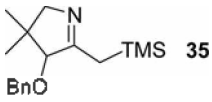
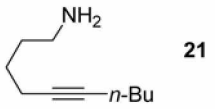
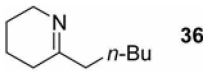
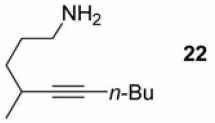
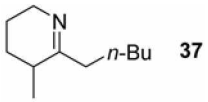
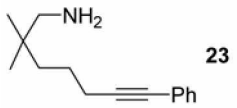
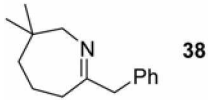
The reaction of **15** with **17** (60 °C, 1.5 h, 1.0 M) afforded **32** in 96% yield (entry 6).

Stimulated by these results, we applied a variety of yttrium-catalysts to intramolecular hydroamination of aminoalkynes to establish the efficiency and scope of the present method. The results are summarized in Table 2. Treatment of **20** with 5 mol% **12**, **13**, and **15** produced **35** in 98% yields (by NMR), respectively, after 0.2 h at 25 °C (entries 10-12). Also, aminoalkyne **18** possessing a methyl group at the carbon attached to nitrogen was smoothly cyclized with **12** to provide **33** in 95% yield (25 °C, 0.2 h, entry 4). These results suggest that cyclization of these substrates would be accellerated by the *gem*-dimethyl effect.[5a] Hydroamination reaction of **18** using **13** and **15** proceeded to give **33** in good yields (entries 5 and 6). Although the reaction of **19** with **12** and **13** afforded the desired product **34** in 92% and 81% yields, respectively, (entries 7 and 8),[10] the use of **15** as a catalyst failed to produce the desired product (entry 9). In addition, exposure of **21** and **22** to **15** did not give the cyclized product (entries 15 and 18). Hydroamination of **22** having a methyl group at the carbon adjacent to the triple bond with **13** proceeded more rapidly to provide **37** in 92% yield [benzene-d_6 at 150 °C for 18 h (entry 17)], while the reaction of **21** with **13** (5 mol%) furnished the cyclized product **36** in 93% yield in C_6D_6 at 150 °C for 71 h (entry 14).[10] Subjecting **23** to **13** (5 mol%) resulted in the production of **38** in 48% yield, albeit under harsh conditions (benzene-d_6, 120 °C, 158 h) (entry 20). The present conditions were ineffective for the secondary amine.

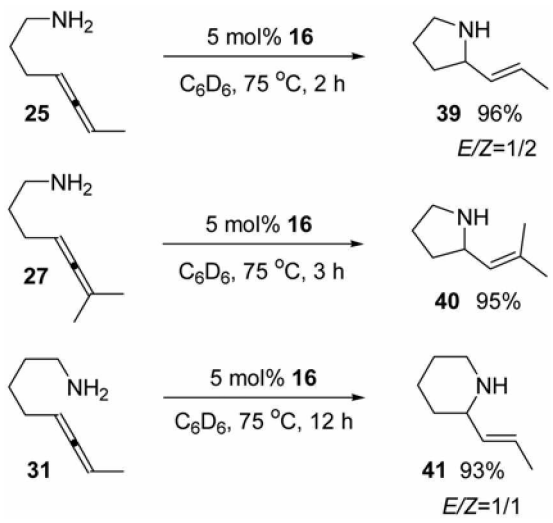
Zirconium-catalyzed Intramolecular Hydroamination of Aminoallenes: Encouraged by yttrium-catalyzed intramolecular hydroamination of aminoalkynes, we next examined the intramolecular hydroamination of aminoallenes (Scheme 6). Reaction of **25** and **27** with 5 mol% **16** afforded 2-(*trans*-1-propenyl)pyrrolidine (**39**) and 2-isopropylenepyrrolidine (**40**) in 96% and 95% yield, respectively. Subjecting **25** to 5 mol% **15** failed to produce the desired product. Exposure of **31** on 5 mol% **16** produced 2-(*trans*-1-propenyl) piperidine (**41**) in 93% yield.

Mechanism: Mechanism of hydroamination reaction involving precatalyst **16** can be suitably observed by ^{31}P NMR. Exposure of **25** on a benzene-d_6 solution of 5mol% **16** resulted in the immediate disappearance of the phosphorus resonance at 75.10 ppm with concomitant appearance of a new signal at 76.58 ppm. The fact that this appeared with the production of Me_2NH on ^1H NMR spectrum is strongly indicative of exchange of the amido ligands at zirconium. Cyclization of **25** at 75 °C over 2 h resulted in 96% conversion to **39** with no change to the ^{31}P resonance at 76.58 ppm, thus providing evidence that the zirconium catalyst is robust under the reaction conditions. Moreover, ^{31}P resonance associated with the free proligand **11** at 89.54 ppm did not appear during this reaction. A plausible mechanistic pathway for the intramolecular hydroamination

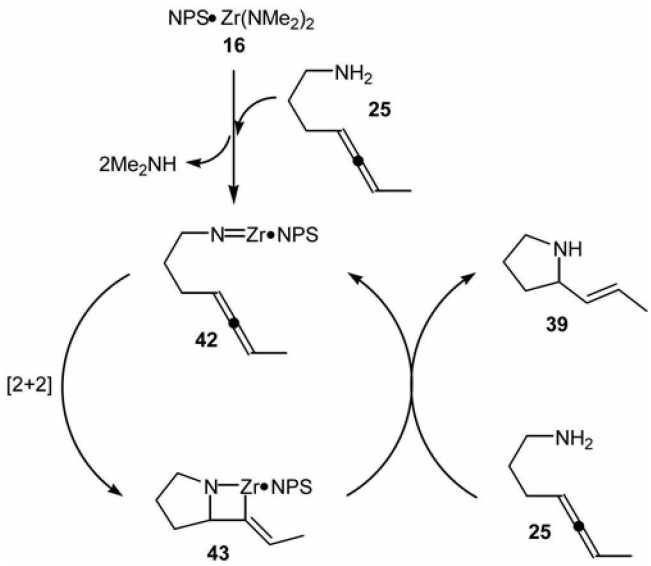
Table 2. Yttrium-catalyzed intramolecular hydroamination of aminoalkynes[a]

Entry	Aminoalkyne	Catalyst	Temp. [°C]	Time [h]	Azacycle	Yield [%][b]
1	 **17**	**12**	60	80	 **32**	96
2		**13**	60	9		94
3		**15**	60	1.5		96
4	 **18**	**12**	25	0.2	 **33**	95
5		**13**	25	1.5		95
6		**15**	75	3		95
7	 **19**	**12**	120	3.5	 **34**	92
8		**13**	120	13		81
9		**15**	120	17		0
10	 **20**	**12**	25	0.2	 **35**	98
11		**13**	25	0.2		98
12		**15**	25	0.2		98
13	 **21**	**12**	150	141	 **36**	67
14		**13**	150	71		93
15		**15**	100	30		0
16	 **22**	**12**	150	20	 **37**	95
17		**13**	150	18		92
18		**15**	150	143		0
19	 **23**	**12**	120	141	 **38**	41
20		**13**	120	158		48
21		**15**	120	21[c]		56

[a]Reaction performed in the presence of 5 mol % catalyst in benzene-d_6 (1.0 M). [b]NMR yields based on *p*-xylene as an internal standard. [c]Days.



Scheme 6. Zirconium-catalyzed intramolecular hydroamination of aminoallenes.



Scheme 7. Proposed mechanism for the hydroamination.

of **25**, involving the putative Zr(IV) imido complex **42**[11] and azazirconacyclobutane **43** based on these observations, is described in Scheme 7.

Conclusions

We have demonstrated that $Y[N(TMS)_2]_3$, the neutral

yttrium-diamine complex **13**, and the yttrium-NPS complex **15** are efficient precatalysts for intramolecular hydroamination of primary aminoalkynes. Complexes **13** and **15** were quantitatively prepared *in situ* by direct metalation reactions of the ligands **4** and **9** with 1 equiv of $Y[N(TMS)_2]_3$ in benzene-d_6 at 120 °C for 5 days and 10 days, respectively, *via* elimination of $(TMS)_2NH$. 5-*Exo*- and 6-*exo-dig* intramolecular hydroamination of aminoalkynes using catalysts **12** and **13** proceeded smoothly to give nitrogen-contained cyclic products in good to excellent yields in all cases. In the case of 7-*exo-dig* intramolecular hydroamination, the desired product was produced in 41% and 48% yields despite the *gem*-dimethyl effect. However, treatment of catalyst **15** with aminoalkynes (**19** and **22**) having a methyl substituent at the carbon adjacent to the triple bond and 6-*exo-dig* intramolecular hydroamination of **21** failed to give the desired products. Zirconium-catalyzed intramolecular hydroamination of aminoallenes **25**, **27**, and **31** with 5 mol% **16** afforded 2-(*trans*-1-propenyl)pyrrolidine, 2-isopropylenepyrrolidine, and 2-(*trans*-1-propenyl)piperidine in 96%, 95%, and 93% yield, respectively. However, subjecting **25** to 5 mol% **15** failed to produce the desired product. Extention of this study is now under investigation in this laboratory.

Experimental

General. Melting points were obtained using a Mel-Temp II apparatus equipped with a digital thermometer and were uncorrected. Infrared spectra were recorded on a Perkin Elmer model 1600 FT-IR. Infrared spectra of solids were obtained by standard KBr pellet procedures. ^{1}H NMR spectra were recorded on a Bruker AVANCE DPX-300 (300 MHz) or AVANCE DPX-500 (500 MHz) spectrometer. J. Young NMR tubes were purchased from Aldrich or J. Young Ltd. Chemical shifts were reported in ppm from tetramethylsilane with the residual protic solvent resonance as the internal standard (chloroform: 7.27, benzene: 7.16, toluene: 7.09). ^{13}C NMR spectra were recorded on a Bruker AVANCE DPX-300 (300 MHz) or AVANCE DPX-500 (500 MHz) spectrometer with complete decoupling. Chemical shifts were reported in ppm from tetramethylsilane with the solvent as the internal standard ($CDCl_3$: 77.23). Analytical thin layer chromatography was performed on Polygram® SIL G/UV_{254} 1.25 mm silica gel plates with a fluorescent indicator. Flash chromatography was performed on Merck silica gel 60. Solvents for extraction and flash chromatography were reagent grade. All experiments were carried out under an argon atmosphere. Organozirconium and organoyttrium complexes were manipulated under an argon atmosphere in a glove box. Benzene-d_6 and toluene-d_8 were distilled from Na and aminoalkynes and aminoallenes were distilled from CaH_2 under an argon atmosphere and stored at −30 °C in a glove box. J. Young NMR tubes, purchased from Aldrich or J. Young Ltd, were used at the corresponding temperature with safety shield.

Preparation of *N,N'*-bis(2-isopropylphenyl)ethane-1,2-diamine (4). To a solution of 2-isopropyl aniline (2.35 g, 17.4 mmol) and triethylamine (2.64 mL, 19.0 mmol) in THF(60 mL) at 0 °C was added dropwise oxalyl chloride (1.0 g, 7.9 mmol). The reaction mixture was stirred overnight and then, refluxed for 1 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (50 mL), and then washed with H_2O (20 mL), 1 N HCl (10 mL), and sat. $NaHCO_3$ (10 mL). The organic layer was dried with anhydrous $MgSO_4$, filtered, and evaporated *in vacuo* to provide *N,N'*-bis(2-isopropylphenyl)oxalamide (2.5 g, 97%) as a white solid (mp = 179-181 °C). *N,N'*-Bis(2-isopropylphenyl)oxalamide (2.0 g, 6.16 mmol) was reduced by addition to $LiAlH_4$ (0.47 g, 12.3 mmol) in THF (30 mL) at room temperature and then, heating the resulting mixture at reflux overnight. The reaction mixture was cooled to 0 °C and carefully quenched *via* sequential addition of H_2O (0.5 mL), 15% aqueous NaOH (0.5 mL) and H_2O (1 mL). The mixture was stirred at room temperature for 2 h, and anhydrous $MgSO_4$ (1.0 g) was added. After filteration, the solvent was evaporated *in vacuo*. The residue was purified by bulb-to-bulb distillation (160-165 °C at 0.5 mmHg) to afford *N,N'*-bis(2-isopropylphenyl)ethane-1,2-diamine (**4**) (1.0 g, 55%) as a white solid (m.p. 47-48 °C). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.15 (m, 4H, ArH), 6.76 (m, 4H, ArH), 4.03 (bs, 2H, NH), 3.50 (s, 4H, CH_2), 2.85 (septet, J = 6.9 Hz, 2H, CH), 1.22 (d, J = 6.9 Hz, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 144.6, 132.8, 126.8, 125.1, 118.0, 110.8, 43.5, 27.2, 22.3; IR(KBr): ν = 3421.3, 2959.5, 2867.5, 1602.3, 1582.1, 1504.7, 1449.1, 1305.6, 1256.8, 744.7 cm^{-1}; HR-MS (CI, NH_3): m/z = 297.2368, exact mass calcd. for $[C_{20}H_{28}N_2H]^-$: 297.2331.

***N,N'*-Bis(2,6-diethylphenyl)ethylenediamine (7).** To a solution of glyoxal (1.14 mL, 9.85 mmol) and 2,6-diethylaniline (3 g, 19.7 mmol) in MeOH (6 mL) was added 2 drops of formic acid and stirred at room temperature overnight. The reaction mixture was concentrated *in vacuo*, and then, the crude compound was directly used for next reaction without further purification. The crude compound dissolved in THF (5 mL) was added dropwise to a suspension of $LiAlH_4$ (750 mg, 19.7 mmol) in THF (80 mL), and then heated at reflux for 1 h. The reaction mixture was cooled to 0 °C and carefully quenched *via* sequential addition of H_2O (1 mL), 15% aqueous NaOH (1 mL) and H_2O (2 mL). The mixture was stirred at room temperature for 1 h and anhydrous $MgSO_4$ (2 g) was added, followed by filtration and concentration of the filtrate *in vacuo*. The residue was purified by distillation (139-149 °C at 1 mmHg) to provide **7** (2.8 g, 88%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.97 (m, 2H, ArH), 3.32 (bs, 2H, NH), 3.10 (s, 4H, NCH_2), 2.62 (q, J = 7.5 Hz, 8H, CH_2), 1.16 (t, J = 7.5 Hz, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 144.9, 136.4, 126.7, 122.9, 50.5, 24.4, 14.9; IR (neat): ν = 3366.9, 2963.4, 2871.1, 1591.9, 1453.9, 1256.3, 1200.1, 1109.9, 754.0 cm^{-1}; LR-MS (EI): m/z (relative intensity) 324 (M^+, 14), 162 (100), 147 (29), 132 (24).

***N,N'*-Bis(*P,P*-diisopropylthiophosphinyl)-2,3-dimethyl-2,3-butanediamine (9).** This compound was prepared in a

fashion analogous to **11** utilizing 2,3-dimethyl-2,3-diaminobutane (0.29 g, 2.5 mmol), 4-methylmorpholine (0.66 mL, 6 mmol), and chlorodiisopropylphosphine (0.8 mL, 5 mmol) in toluene (15.5 mL) at 70 °C, followed by the addition of sulfur (0.17 g, 5.25 mmol). The residue was purified by column chromatography on silica gel to give **9** (440 mg, 43%), using CH_2Cl_2 for elution. m.p. 147-148 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.69 (bs, 2H, NH), 2.19 (septet, J = 6.9 Hz, 4H, CH), 1.44 (s, 12H, CH_3), 1.22 (d, J = 6.9 Hz, 12H, CH_3), 1.19 (d, J = 6.9 Hz, 12H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 62.5 (d, J_{c-p} = 5.0 Hz), 31.4 (d, J_{c-p} = 67.3 Hz), 25.0, 17.2, 16.5; ^{31}P NMR (121 MHz, $CDCl_3$, 25 °C): δ = 83.59; IR (KBr): ν = 3319.9, 3240.3, 2961.2, 1458.8, 1420.8, 1135.9, 1021.5, 690.2 cm^{-1}; HR-MS (EI): m/z = 412.2256, exact mass calcd. for $[C_{18}H_{42}N_2P_2S_2]^+$: 412.2264.

Synthesis of *N,N'*-bis(*P,P*-diisopropylthiophosphinyl)-2,2-dimethyl-1,3-propanediamine (11). To a solution of 2,2-dimethylpropane-1,3-diamine (255.0 mg, 2.5 mmol) and *N,N*-diisopropyl-ethylamine (1.96 mL, 11.3 mmol) in dichloromethane (5 mL) was added dropwise chlorodiisopropylphosphine (0.8 mL, 5.0 mmol) dissolved in dichloromethane (3 mL) with stirring at 0 °C. The reaction mixture was allowed to warm to 25 °C and it was stirred overnight. Sulfur (170.0 mg, 5.3 mmol) was added in small portions to the resulting mixture. The reaction mixture was stirred for 2 h at room temperature and then, it was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to give **11** (710.0 mg, 72%), using 20% ethyl acetate in *n*-hexane for elution. Recrystallization from methylcyclohexane gave **11** (670.0 mg, 68%) as a white solid (m.p. 143-144 °C). ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 2.95 (t, J = 8.0 Hz, 4H, CH_2), 2.67 (q, J = 8.0 Hz, 2H, N*H*), 2.10 (septet, J = 7.0 Hz, 4H, C*H*), 1.11 (d, J = 7.0 Hz, 6H, CHCH_3), 1.07 (t, J = 5.75 Hz, 12H, CHCH_3), 1.03 (d, J = 7.0 Hz, 6H, CHCH_3), 0.82 (s, 6H, C(CH_3)$_2$); ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ = 47.4, 31.1, 30.6, 24.1, 17.0, 17.0; ^{31}P NMR (121 MHz, C_6D_6, 25 °C): δ = 89.54; IR (KBr) ν = 3324.3, 3207.0, 2974.0, 1446.5, 1073.8, 829.8, 708.4 cm^{-1}; HR-MS (EI): m/z = 398.2097, exact mass calcd. for $[C_{17}H_{40}N_2P_2S_2]^+$ 398.2108.

Typical procedure for intramolecular hydroaminations of aminoalkynes using yttrium complexes 13. In an argon-filled glove box, Y[N(TMS)$_2$]$_3$ (11.4 mg, 0.02 mmol) and *N,N'*-bis(2-isopropylphenyl)ethane-1,2-diamine (**4**) (5.93 mg, 0.02 mmol) in C_6D_6 (0.4 mL) were introduced sequentially into a J. Young NMR tube with Teflon screw cap purchased from Aldrich or J. Young Ltd. The reaction mixture was stirred at 120 °C for 5 days until ligand attachment was judged completely by the disappearance of the Y[N(TMS)$_2$]$_3$ with concomitant generation of the free (TMS)$_2$NH. The appropriate aminoalkynes (0.4 mmol) and and *p*-xylene (4.9 mL, 0.04 mmol) were added to the resulting complex *via* microsyringe and the reaction mixture was subsequently heated at corresponding temperature in an oil bath untill hydroamination was judged complete by disappearance of the starting metarial in the ^{1}H-NMR relative to the aromatic resonance of the internal standard *p*-xylene.

Typical procedure for intramolecular hydroaminations of aminoalkynes using yttrium complexes 15. In an argon-filled glove box, Y[N(TMS)$_2$]$_3$ (11.4 mg, 0.02 mmol) and *N,N'*-bis(*P,P*-diisopropylthiophosphinyl)-2,3-dimethyl-2,3-butanediamine (**9**) (8.25 mg, 0.02 mmol) in C_6D_6 (0.4 mL) were introduced sequentially into a J. Young NMR tube with Teflon screw cap. The reaction mixture was stirred at 120 °C for 10 days until ligand attachment was judged completely by the disappearance of the Y[N(TMS)$_2$]$_3$ with concomitant generation of the free (TMS)$_2$NH. The appropriate aminoalkynes (0.4 mmol) and and *p*-xylene (4.9 mL, 0.04 mmol) were added to the resulting complex *via* micro syringe and the reaction mixture was subsequently heated at corresponding temperature in an oil bath untill hydroamination was judged complete by disappearance of the starting metarial in the ^{1}H-NMR relative to the aromatic resonance of the internal standard *p*-xylene.

Zr(IV) bis(thiophosphinic amidate) complex (16). In an argon-filled glove box, Zr(NMe$_2$)$_4$ (20 μL, 0.02 mmol, 1.0 M solution in benzene-d_6 or toluene-d_8) and *N,N'*-bis(*P,P*-diisopropylthiophosphinyl)-2,2-dimethyl-1,3-propanediamine (7.97 mg, 0.02 mmol) in C_6D_6 (0.4 mL) or toluene-d_8 (0.4 mL) were introduced sequentially into a J. Young NMR tube. The reaction mixture was stirred at 25 °C for 10 min until ligand attachment was judged completed by the disappearance of the Zr(NMe$_2$)$_4$ resonance in the ^{1}H NMR spectrum with concomitant production of Me$_2$NH. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ = 3.11 (s, 12H, Zr[N(CH_3)$_2$]$_2$), 2.69 (d, J = 10.0 Hz, 4H, CH_2), 1.99 (septet, J = 7.25 Hz, 4H, C*H*), 1.16 (d, J = 7.0 Hz, 6H, CHCH_3), 1.13 (dd, J = 7.0 Hz, J = 1.5 Hz, 12H, CHCH_3), 1.09 (d, J = 7.0 Hz, 6H, CHCH_3), 0.89 (s, 6H, C(CH_3)$_2$); ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ = 57.9, 44.1, 29.1, 28.7, 26.4, 17.7, 16.7; ^{31}P NMR (121 MHz, C_6D_6, 25 °C): δ = 75.10; Elemental analysis calcd. (%) for $C_{21}H_{50}N_4P_2S_2Zr$: C 43.79, H 8.75, N 9.73; found: C 43.74, H 8.73, N 9.69.

Typical procedure for intramolecular hydroaminations of aminoallenes using NPS·Zr(NMe$_2$)$_2$ complexes (16). In an argon-filled glove box, Zr(NMe$_2$)$_4$ (20 μL, 0.02 mmol, 1.0 M solution in benzene-d_6) and *N,N'*-bis(*P,P*-diisopropylthiophosphinyl)-2,2-dimethyl-1,3-propanediamine (7.97 mg, 0.02 mmol) in benzene-d_6 (0.4 mL) or toluene-d_8 (0.4 mL) were introduced sequentially into a J. Young NMR tube. The reaction mixture was stirred at 25 °C for 10 min until ligand attachment was judged completed by the disappearance of the Zr(NMe$_2$)$_4$ resonance in the ^{1}H NMR spectrum with concomitant production of Me$_2$NH. The appropriate aminoallene (0.40 mmol) and *p*-xylene (10.0 μL, 0.08 mmol) were added to the resulting solution and then, the reaction mixture was subsequently heated at 75 °C in an oil bath to achieve hydroamination.

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