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Group-4 Dipyrrolylmethane Complexes in Intramolecular Olefin Hydroamination

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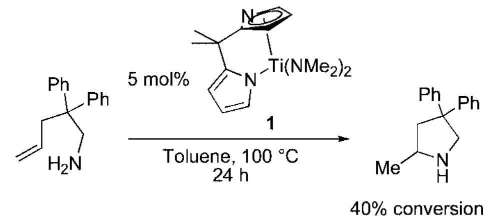
Titanium and zirconium complexes bearing the 5,5-dimethyldipyrrolylmethane (dpm) ancillary ligand were tested for their activity in intramolecular hydroamination of olefins. The titanium precatalyst $Ti(NMe_2)_2(dpm)$, despite being an excellent catalyst for intermolecular alkyne hydroamination, was a relatively poor catalyst for intramolecular olefin hydroamination. The zirconium derivative was significantly more active. With a secondary amine, $[Zr(NMe_2)_2(dpm)]_2$ did catalyze the hydroamination reaction, albeit slowly. Consequently, the mechanism of the reaction with zirconium may use a 1,2-insertion into a Zr−N amido bond as the key mechanistic step, or the complex may be able to access both the [2 + 2]-cycloaddition and 1,2-insertion mechanisms. The zirconium precatalyst was structurally characterized by X-ray diffraction and is a dimer in the solid state, but solution molecular weight determination gave results closer to the monomer in benzene.

Intramolecular hydroamination[1] of olefins is a reaction of great potential utility in the formation of heterocycles. A plethora of complexes, many involving group 3 or lanthanides[2,3] in addition to group 4[3,4] metals, have been explored as catalysts for this reaction. Many of the known catalysts for intramolecular hydroamination are believed to use either a [2 + 2]-cycloaddition[5] or 1,2-insertion[6,1c] route; these are illustrated in Scheme 1.

In previous hydroamination research, our group has explored the use of pyrrolyl-based ancillary ligands in intermolecular alkyne hydroamination.[7] While this reaction is also of great potential utility, it was thought that catalyst development for intermolecular hydroamination of alkynes may provide clues as to catalyst development for intermolecular olefin hydroamination of unactivated olefins, a reaction for which there are as yet no general catalysts. Here, we report the results of intramolecular olefin hydroamination studies using a very rapid alkyne hydroamination precatalyst, η^5,η^1-(5,5-dimethyldipyrrolylmethane)bis(dimethylamido)titanium(IV), or $Ti(dpm)(NMe_2)_2$ (**1**).[7a] In addition, we report the synthesis, structure, and catalytic reactivity of its zirconium derivative.

Reaction of 2,2-diphenylpent-4-en-1-amine with 5 mol% **1** in toluene was carried out at temperatures up to 100 °C (eq 1). This complex, which can catalyze the reaction of many alkynes and primary amines rapidly even at room temperature, reacted only slowly with this alkene substrate, reaching 40% conversion after 24 h.



(1)

The low reactivity of the titanium complex led us to prepare the zirconium derivative, reasoning its larger ionic radius would perhaps lead to increased activity with these olefin substrates. The zirconium derivative (**2**) was prepared according to eq 2.

X-ray diffraction on a sample of the complex revealed the compound to be an unusual dimer in the solid state. The structure found for the complex is bis(μ^2:η^1,η^5-5,5-dimethyl-

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(5) (a) Walsh, P. J.; Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 5459. (b) Baranger, A. M.; Walsh, P. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 2753.

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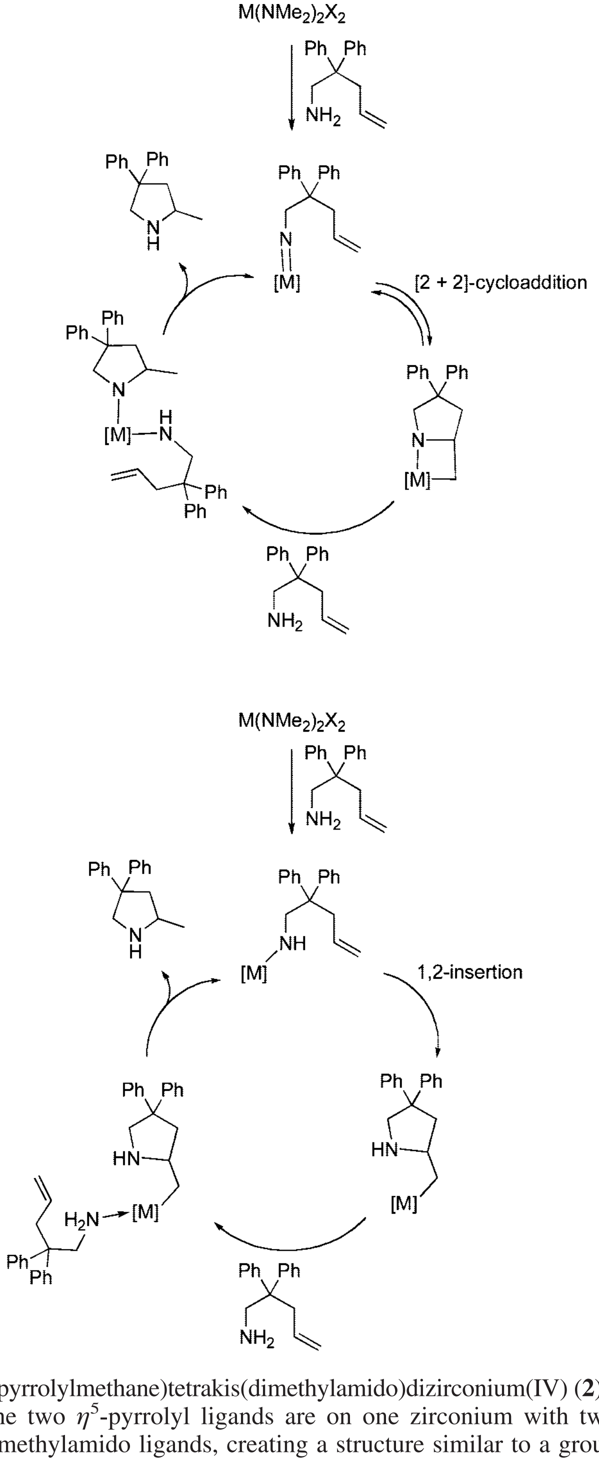
10.1021/om700883a CCC: $40.75

Scheme 1. [2 + 2]-Cycloaddition Mechanism of Bergman (top) and the 1,2-Insertion Mechanism of Marks (bottom)



dipyrrolylmethane)tetrakis(dimethylamido)dizirconium(IV) (**2**).[8] The two η^5-pyrrolyl ligands are on one zirconium with two dimethylamido ligands, creating a structure similar to a group 4 metallocene. The other zirconium center is coordinated to two dimethylamidos, two η^1-pyrrolyls, and the two nitrogens of the η^5-pyrrolyl ligands facially bound to its cohabitant zirconium. Consequently, one of the zirconium atoms in the complex is pseudo-octahedral, and there is an approximate 2-fold axis along the Zr−Zr vector (Figure 1). The structure in solution, as judged by NMR spectroscopy, is consistent with the solid-state structure. However, considering the titanium derivative **1** has

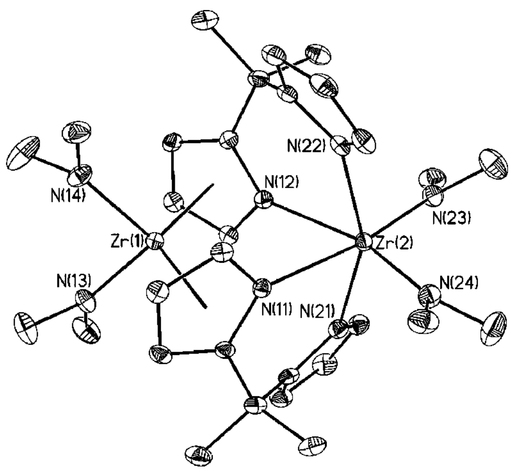
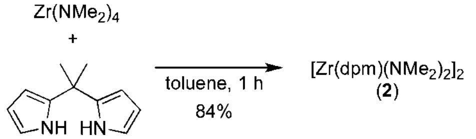


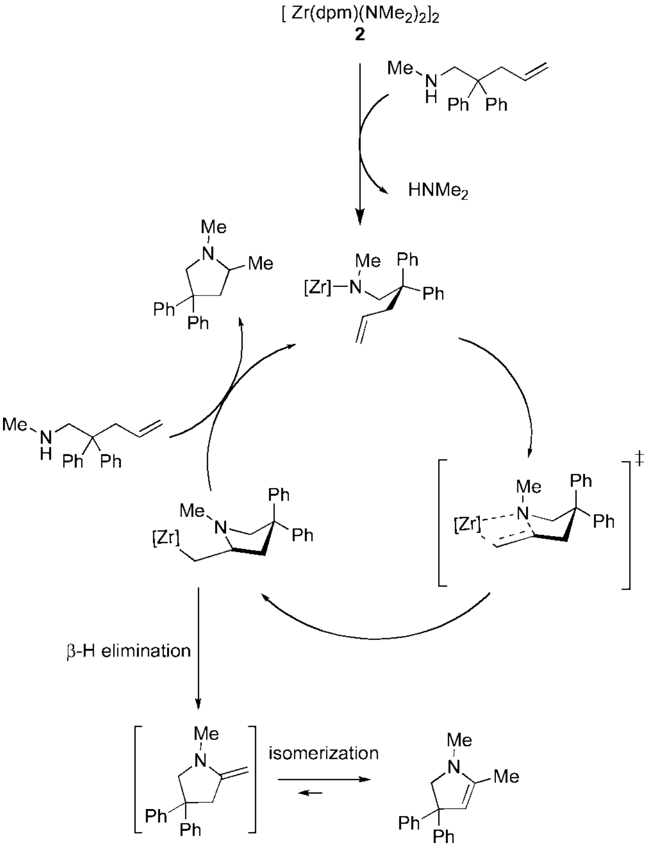
Figure 1. Structure of [Zr(dpm)(NMe$_2$)$_2$]$_2$ (**2**) by X-ray diffraction. Selected distances (Å): Zr(1)−N(13) 2.049(4), Zr(2)−N(23) 2.060(4), Zr(1)−N(11) 2.515(3), Zr(2)−N(11) 2.404(3), Zr(2)−N(21) 2.232(4), Zr(1)−C(111) 2.615(4). Selected angles (deg): N(14)−Zr(1)−N(13) 94.9(2), N(23)−Zr(2)−N(24) 101.9(2), N(23)−Zr(2)−N(12) 97.4(1), N(12)−Zr(2)−N(22) 80.0(1), N(12)−Zr(2)−N(11) 73.0(1), N(11)−Zr(2)−N(22) 81.0(1).



(2)

an η^1,η^5-dpm in the solid state and solution, the (η^1,η^5-5,5-dimethyldipyrrolylmethane)bis(dimethylamido)zirconium(IV)

Scheme 2. Possible Route to the Product Distribution Observed when *N*-Methyl-2,2-diphenylpent-4-en-1-amine Is Reacted with 2



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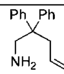
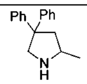
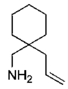
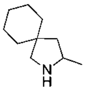
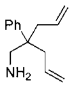
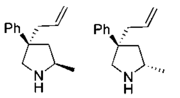
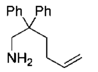
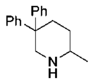
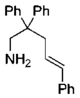
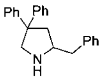
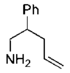
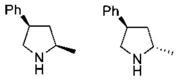
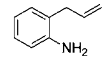
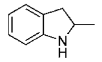
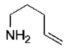
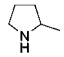
[8] Monoclinic $P2(1)/n$; $a = 10.892(3)$ Å, $b = 16.012(4)$ Å, $c = 18.471(5)$ Å, $b = 100.392°$; reflections total/unique = 26 880/4578 [R. (int) = 0.0492] for 362 parameters; goodness-of-fit = 1.045; R1 [$I > 2\sigma$] = 0.0349, wR2 [$I > 2\sigma$] = 0.0905; R1 [all data] = 0.0437, wR2 [all data] = 0.0947.

Table 1. Catalytic Intramolecular Hydroamination Reactions with Zirconium Catalysts[a]

Entry	Aminoalkene	Product	Time (h)	Temp (°C)	**2**	$Zr(NMe_2)_4$
					%Conv(%yield)[b]	%Conv(%yield)[b]
1			1	100	100 (92)	92
2			3	100	100 (86)	100
3		 1:1	3	100	100 (96)	100
4			15	100	100	100 (83)[c]
5			96	110	55	100 (87)
6		 1:1	120	150	93 (57)	97
7			96	150	92 (73)	--[d]
8			28	150	--[c]	25

[a] 2.5 mol% $[Zr(dpm)(NMe_2)_2]_2$ (**2**) or 5 mol% $Zr(NMe_2)_4$ in toluene. [b] % conversion by GC/FID and % isolated yield. [c] Reaction time was 3 h. [d] Some product observed but not a clean reaction. [e] Hydroamination product not observed.

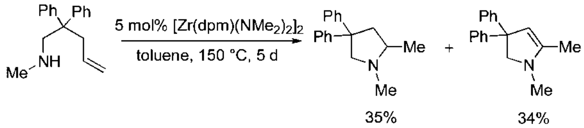
monomer, and the dimeric structure observed in the solid state may be difficult to distinguish by NMR alone.

There is some evidence that this dimer is relatively easy to convert to the two monomers. An EI-MS experiment on the solid complex resulted in the monomer being the highest molecular weight observed. The solution molecular weight of the complex, determined cryogenically in benzene, was consistently between monomer and dimer, favoring the monomer.

The zirconium derivative is significantly more active in intramolecular olefin hydroamination than the titanium complex, and the results with several substrates are shown in Table 1. As is often the case in intramolecular hydroamination, substitution in the chain between the olefin and amine is greatly advantageous, the "reactive rotamer" effect.[9] Attempts to convert less substituted pent-4-en-1-amine to 2-methylpyrrolidine resulted in no reaction (entry 8, Table 1). Catalytic reactions involving **2** to form six-membered rings (entry 4) and to react with *trans*-disubstituted olefins (entry 5) were not as rapid as with $Zr(NMe_2)_4$. Diasteriometric ratios were found to be ~1:1, where applicable.

In general, $Zr(NMe_2)_4$ was a comparable catalyst to the pyrrolyl complex **2**. Complex **2** was significantly better for the aryl derivative shown in entry 7. For the substrate without branching (entry 8, Table 1), $Zr(NMe_2)_4$ is a reasonably effective catalyst giving 25% under these conditions but full conversion at higher concentrations.[4i] This is, again, in contrast to the titanium alkyne catalysis chemistry where $Ti(NMe_2)_2(dpm)$ (**1**) is noticeably faster than $Zr(NMe_2)_4$.[7a]

Most neutral group 4 complexes are believed to use the [2 + 2]-cycloaddition mechanism (Scheme 1).[10] However, reaction of *N*-methyl-2,2-diphenylpent-4-en-1-amine with 5 mol% $[Zr(dpm)(NMe_2)_2]_2$ (**2**) results in formation of compounds consistent with hydroamination. Since it is highly unlikely that an imido-based mechanism could be operative in eq 3, a 1,2-insertion route is favored. The reaction is significantly slower than in the related primary amine ring closure (entry 1, Table 1).



(3)

A reaction under similar conditions utilizing the secondary amine substrate in eq 3 and $Zr(NMe_2)_4$ resulted in production

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(9) Jung, M. E.; Piizzi, G. *Chem. Rev.* **2005**, *105*, 1735–1766. See especially: Brown, R. F.; van Gulick, N. M. *J. Org. Chem.* **1956**, *21*, 1046–9.

(10) It has been reported recently that neutral zirconium "constrained-geometry" catalysts use the 1,2-insertion pathway: Stubbert, B. D.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 6149–67.

of the hydroamination product with full conversion after 12 h. The dehydrogenated product was not observed. This secondary amine does not undergo cyclization with added $Ti(NMe_2)_4$ under these conditions, and starting material is recovered.[4h]

A possible route for generating these products would involve β-hydride elimination and zirconium alkyl protonolysis after olefin insertion into a Zr−N bond.[11] The enamine product was observed by ^1H NMR and GC/MS; however, it was not isolable as a pure compound from the pyrrolidine.[12] Consequently, the yield given for the enamine is approximate, based on the GC-FID response of the isolable pyrrolidine.

These results suggest that $[Zr(dpm)(NMe_2)_2]_2$ (**2**) uses 1,2-insertion either exclusively or in concert with the [2 + 2]-cycloaddition pathway. However, the neutral zirconium complexes reported to use this mechanism by Marks did not seem to have significantly different activity with primary and secondary amines as seen for **2**.[10] Whether this indicates that **2** can access both mechanisms with the [2 + 2]-cycloaddition route being lower in energy will require further study. Currently, there are several intriguing mechanistic possibilities, including possible differing routes for the monomer and dimer in solution.

While the excellent intermolecular alkyne hydroamination catalyst $Ti(dpm)(NMe_2)_2$ is a poor catalyst for intramolecular alkene reactions, the zirconium derivatives look promising. Substitutions within the dipyrrolylmethane framework may be fruitful for catalyzing these intramolecular hydroaminations.

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Supporting Information Available: Detailed conditions for hydroamination reactions, product characterization data, NMR spectra, and tables from the X-ray diffraction experiment on **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Several control experiments were run on the reaction in eq 3. No reaction was observed in the absence of catalyst. Addition of bases to the reaction, to rule out proton involvement, was also investigated. The reaction was run under the same conditions with either 2,6-di-*tert*-butyl-4-methylpyridine or tris(*n*-octyl)amine (1 equiv with respect to amine substrate). Neither base had a noticeable effect on the yield or selectivity of the reaction.

(12) A report of a closely related enamine suggests it may be unstable under typical workup conditions: Pugin, B.; Venanzi, L. M. *J. Am. Chem. Soc.* **1983**, *105*, 6877–81.