Hydroamination of Alkynes Catalyzed by Imido Complexes of Titanium and Vanadium

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Intermolecular alkyne hydroamination with primary amines is catalyzed with group 5 (vanadium and tantalum) transition metal complexes and a new imido-Ti(IV) complex. The reaction is very regioselective. The scope of the reaction was investigated with a variety of alkynes and amines; 1-hexyne and anilines were found to be especially good substrates.

Introduction

N-containing molecules such as amines, imines, and enamines are among the most important chemical substances, playing key roles as biologically active compounds and as bulk and fine chemicals.[1] The direct hydroamination of alkynes with primary amines constitutes a perfect atom economy reaction[2] for the synthesis of such N-containing molecules, as imines are formed in a single step without formation of byproducts. For that reason, research of new homogeneous catalysts for alkyne hydroamination is currently a field of intense activity. The homogeneously catalyzed hydroamination of alkynes is known to proceed in the presence of many catalysts[3] (mercury and thalium salts,[4] alkaly metals,[5] lanthanides,[6] actinides,[7] zirconium,[8] ruthenium,[9] rhodium,[10] palladium,[11] and gold[12] complexes), but cheap and easily available titanium complexes are now among the most studied due to their rapidity, regioselectivity, and ease of use for that reaction.[13−17]

Our group has been interested in titanium[18] and vanadium[19] chemistry for many years, in particular through the development of new vanadium-based catalysts for olefin polymerization.[18a,b,d,19h] Furthermore, we have developed simple routes to a series of new imido-vanadium(IV)[19a,b,h] and -titanium(IV) complexes, and since group 4 metal-imido intermediates are considered to be the catalytically active species in Ti- and Zr-catalyzed alkyne hydroamination reactions,[17] we became particularly interested in studying the potentiality of our imido complexes as alkyne hydroamination catalysts as well as to screen various vanadium precatalysts. Surprisingly, only very few studies have been carried out using directly a group 4 metal-imido catalyst, all bearing an additional Cp[13e,17a−c] co-ligand, with the exception of Richeson's guanidinate-supported titanium

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imido complex, which is an active alkyne hydroamination catalyst,[15a] and the very recent and interesting work conducted by Bergman et al.[15d] on titanium bis-(sulfonamido) complex $LTi(NMe_2)_2$ as an allene hydroamination catalyst. This latter complex was shown to form the imido complex $LTi(=NAr)(Py)$ (Ar = 2,6-$Me_2C_6H_3$) when reacted with $2,6-Me_2C_6H_3NH_2$ in the presence of pyridine, and the authors briefly report the intramolecular allene hydroamination with this imido species to have a rate similar to that observed using the parent precatalyst. Moreover, no activity was found in the only reported study on alkyne hydroamination with an imido complex that does not have an additional Cp or guanidinate co-ligand (namely, $Ti(OAr)_2(NPh)$-$(Py')_2$, Ar = $2,6-Ph_2C_6H_3$, Py' = 4-pyrrolidinopyridine).[15c] It is also important to note that so far no activity has been reported for any group 5 transition metal compound. In this article, we describe Ti-, V-, and Ta-based catalysts for the direct addition of primary amines to unactivated alkynes.

Results and Discussion

1. Hydroamination of 1-Hexyne and Aniline. Screening of New Catalysts. Catalytic reactions were carried out using screw cap vials in an oil bath maintained at 80 °C, in toluene solvent with 0.2 mmol of catalyst (i.e., 10 mol %, but lower amounts have been used (2 mol %)), and with a slight excess of amine (typically, 1.5 equiv of amine and 1 equiv of alkyne).[20] The reaction progress was monitored by gas chromatography.

Since commercially available $Ti(NMe_2)_4$ has proven to be a precatalyst for the hydroamination of some alkynes,[16a] we first tested the vanadium analogue $V(NMe_2)_4$ (**1**) for the hydroamination of a test substrate combination composed of 1-hexyne and aniline. The results are shown in Table 1 together with a comparison versus $Ti(NMe_2)_4$ (**4**) under the same conditions.

Catalytic 1-hexyne hydroamination with **1** proceeds to give reasonable yields but with slower rates as compared to **4** (**1**: 60% of imine formed in 20 h; **4**: 90% in less than 4 h). Nevertheless, V-based catalyst **1** is much more regioselective, as the Markovnikov product is almost the exclusive product (M:AM = 98:2 for **1** and 65:35 for **4**).

A large number of titanium complexes catalyze alkyne hydroamination; to probe the scope of the vanadium-catalyzed reaction, we tested several different vanadium complexes. Unfortunately, most of them were inactive (namely, Cp_2V, $V(acac)_3$, $VO(acac)_2$, $V(N_3)_2(NMe_2)_2$, $V(O^iPr)_4$, $VO(OR)_3$ (R = ^iPr; $CH_2CF)_3$, $VO(NEt_2)_3$, $V(NAr)Cl_3$ (Ar = $2,6-^iPr_2-C_6H_3$))[21] or gave a very low yield of imine ($[V(NEt_2)_2(THF)][B(C_6F_5)_4]_2$: 11% of imine formed after 20 h, 50% alkyne recovery; $V(N(SiMe_3)_2)_3$: 22% of imine formed after 17 h, 8% alkyne recovery).

Table 1. Intermolecular Hydroamination of 1-Hexyne with Aniline in the Presence of Vanadium, Titanium, and Tantalum Catalysts[a]

catalyst	time (h)[b]	yield imine (%)[c]	selectivity (M:AM)[d]	alkyne recovery (%)
$V(NMe_2)_4$ (**1**)	20	60	98:2	0
$V(carb)_2(NMe_2)_2$ (**2**)	20	79	99:1	0
$[V(\mu^2-NPh)(NMe_2)_2]_2$ (**3**)	20	85	99:1	0
$Ti(NMe_2)_4$ (**4**)	4	90	65:35	0
$[Ti(NPh)(NHPh)_2]$ (**5**)	2	94	80:20	0
$Ti(NPh)Cl_2(NHMe_2)_2$ (**6**)	22	35	45:55	60
$Ta(NMe_2)_5$ (**7**)	20	34	78:22	51

[a] Conditions: catalyst 0.2 mmol (except for the dimer **3**: 0.1 mmol), 1-hexyne 2 mmol, aniline 3 mmol, toluene 5 g, 80 °C. Reaction conditions are not optimized. [b] The reaction time has not been minimized. [c] Yields were obtained by GC analysis vs dodecane internal standard. [d] Ratio Markovnikov to anti-Markovnikov imine products by GC.

By contrast Cp_2VMe_2 did not give imine product, but instead we observed the cyclotrimerization of 1-hexyne (1-hexyne conversion: 40% in 20 h) leading to the formation of two isomers of tri-*n*-butylbenzene as the only detectable products (**A** = $1,3,5-^nBu_3-C_6H_3$ and **B** = $1,3,4-^nBu_3-C_6H_3$ in a ratio **A**:**B** = 35:65). Similarly, we observed the almost complete conversion of phenylacetylene with formation of only trace amounts of imine products, while it reacted with aniline and Cp_2VMe_2 (at 100 °C for 24 h); in that case cyclotrimers of phenylacetylene were not observed, resulting presumably in the formation of higher oligomers. Indeed, dimerization, cyclotrimerization, oligomerization, or polymerization of terminal alkynes is known to proceed with titanium or zirconium compounds.[22] Attempts of hydroamination of internal alkynes (such as diphenylacetylene or 3-hexyne) with aniline and Cp_2VMe_2 (at 100 °C for 24 h) resulted in the formation of only trace amounts of the corresponding imines. Thus, the behavior of Cp_2VMe_2 is in contrast with Cp_2TiMe_2, which catalyzes alkyne hydroamination reactions.[13a,d]

Other vanadium complexes were found to catalyze 1-hexyne hydroamination (Table 1). $V(carb)_2(NMe_2)_2$ (**2**) (carbH = carbazole), prepared by reaction of 2 equiv of carbazole with **1** at room temperature (an X-ray structure determination was realized, see the ORTEP drawing in Figure 1 with selected bond parameters), gave after 20 h at 80 °C slightly higher yield of Markovnikov imine (79%, M:AM = 99:1) than that obtained using **1**.[23] This suggests that the amido carbazole function certainly remains attached to the metal during the catalytic cycle; however it has not yet been verified by experimental data.

(20) It has been shown on alkyne hydroamination using $Ti(NMe_2)_4$ that a larger excess of aniline (3 equiv) vs alkyne (1 equiv) gives faster rates; see ref 16a (we experimentally verified this point on $Ti(NMe_2)_4$). However, with our vanadium catalysts, the effect of a larger excess of aniline is less important.

(21) If we assume that an imido functionality is the key intermediate for vanadium-catalyzed alkyne hydroamination (as demonstrated with titanium catalysts), we believe that some of these vanadium complexes are inactive probably because the imido function is not generated in-situ in the presence of aniline.

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(23) Furthermore, a comparison of the reaction progress (monitored by GC) has also shown complex **2** to be a slightly faster precatalyst than **1**.
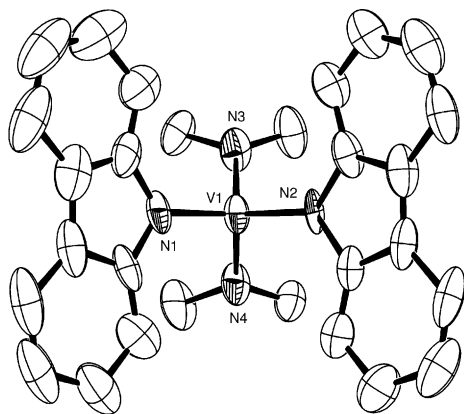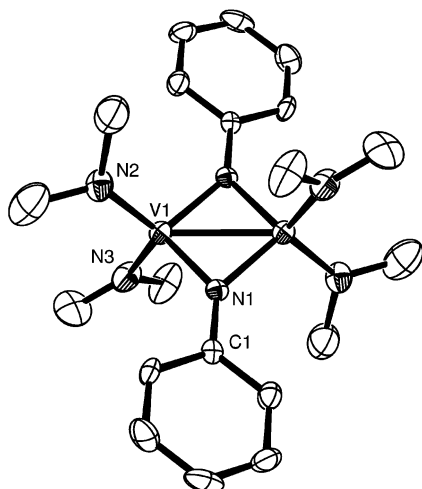
Figure 1. ORTEP drawing of the molecular structure of **2** showing 50% probability ellipsoids and partial atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): V1−N1 1.930(10), V1−N2 1.917(7), V1−N3 1.811(10), V1−N4 1.816(10), N1−V1−N2 107.9(4), N1−V1−N3 111.0(5), N1−V1−N4 110.2(4), N2−V1−N3 111.5(4), N2−V1−N4 111.3-(4), N3−V1−N4 105.0(6).

Figure 2. ORTEP drawing of the molecular structure of **3** showing 50% probability ellipsoids and partial atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): V1−N1 1.867(4), V1−N2 1.838(5), V1−N3 1.810(5), N1−C1 1.405-(6), V1−V1′ 2.493(5), V1−N1−C1 138.7(3).

The imido complex $[V(\mu^2\text{-NPh})(NMe_2)_2]_2$ (**3**) was synthesized by a procedure described earlier[19b] by addition of 1 equiv of aniline to **1** in toluene at 100 °C. The crystal structure of **3** has recently been solved, and an ORTEP drawing is depicted in Figure 2 with selected geometric parameters (the molecular structure of **3** appears to be similar to those of other imido-bridged vanadium complexes described in previous articles[19b] and therefore will not be discussed here). Not surprisingly, compound **3** is the better hydroamination V-based catalyst so far tested, with 85% yield of almost exclusively Markovnikov imine.[24] Nevertheless, the reaction remains slower than that with **4**.

As previously pointed out, very few studies have been conducted using titanium (or zirconium) complexes that already possess the putative imido function,[8c,d,13e,15a,17a−c] and in particular there is no report on an isolated simple imido complex without Cp or guanidinate co-ligand that catalyzes alkyne hydroamination. As a consequence, it would be of great interest to test simple imido-titanium complexes for 1-hexyne hydroamination. Unfortunately, the simplest imido-titanium complex $[Ti(\mu^2\text{-NPh})\text{-}(NMe_2)_2]_2$, analogous to the vanadium compound **3**, was not accessible by the direct reaction between **4** and 1 equiv of PhNH$_2$.[25] Nevertheless, by reacting 3 equiv of PhNH$_2$ with **4** in toluene at 110 °C overnight, we obtained the red microcrystalline complex [Ti(NPh)-(NHPh)$_2$] (**5**) in good yield.[26] Furthermore, **5** might well represent the real active species in alkyne-aniline hydroamination with Ti(NMe$_2$)$_4$ under catalytic conditions.[27] Effectively, **5** appeared to be an extremely efficient catalyst for 1-hexyne hydroamination, which yielded in less than 2 h 94% of imine with a selectivity M:AM ratio of 80:20.

We also used the imido complex Ti(NPh)Cl$_2$(NHMe$_2$)$_2$ (**6**),[28] which was prepared by a procedure similar to that used for the preparation of the vanadium analogue V(NPh)Cl$_2$(NHMe$_2$)$_2$.[19b] The slow hydroamination process observed with **6** (only 35% of imine products formed after 22 h) is probably attributable to the detrimental effect of chlorine atoms at the metal center, which affects the electronic properties of the catalyst.

Finally, Ta(NMe$_2$)$_5$ (**7**)[29] was used to perform 1-hexyne hydroamination under the same conditions used for titanium and vanadium catalysts. A slow, but nonnegligeable, catalytic reaction occurred with formation of 34% imine, with Markovnikov regioselectivity (M:AM = 78:22).

2. Hydroamination of Other Alkynes. We selected two imido complexes, **3** and **5**, to further evaluate their catalytic activity toward the hydroamination of other alkynes with aniline. All these reactions were done with 10 mol % catalyst at 100 °C and were stopped after 24 h; the reaction times were not optimized.

(24) A series of other imido-vanadium(IV) complexes have been, or are being, tested for alkyne hydroamination. In general imido-amido complexes give results similar to that obtained with catalyst **3**; for example the new complex [V(NPh)(NHPh)$_2$] produced 85% of imine (M:AM 99:1) in 20 h.

(25) In our hands, reaction of Ti(NMe$_2$)$_4$ with 1 equiv of PhNH$_2$ at 100 °C gives a mixture of imido complexes from which we have isolated complexes (oligomers) that have a ratio Ti/(NPh) < 1 (unpublished results). Recently, other authors have described the same reaction but at room temperature leading to the tetramer [(Me$_2$N)$_6$Ti$_4$(μ-NPh)$_5$]. See: Fan, M.; Duesler, E. N.; Paine, R. T. *Appl. Organomet. Chem.* **2003**, *17*, 549.

(26) Complex **5** is insoluble in most common organic solvents, suggesting that it might probably be an oligomeric material of the type [Ti(NPh)(NHPh)$_2$]$_n$. Work is in progress to synthesize analogue complexes with other functionalized anilines that might give more soluble, easier to characterize, compounds. The insolubility of **5** is not a restriction for its use as hydroamination catalyst, as **5** does solubilize in the catalytic medium. One proof of the presence of an imido function in **5** is its reactivity toward C=O bonds of carbonyl compounds (acetone-d_6 and benzophenone), via metathesis, which provides the corresponding imines and titanium oxides.

(27) We used in this paper a ratio PhNH$_2$/catalyst of 15, and Odom used a ratio of 30 (see also refs 16a and 20).

(28) Complex **6** was prepared by a very convenient one-pot reaction between Ti(NMe$_2$)$_4$ (1 equiv), PhNH$_2$ (1 equiv), and Me$_3$SiCl (8 equiv) in toluene (80 °C) (C. Lorber, unpublished results). This complex has previously been prepared by a different route starting from TiCl$_2$-(NMe$_2$)$_2$ and PhNH$_2$: Adams, N.; Cowley, A. R.; Dubberley, S. R.; Sealey, A. J.; Skinner, M. E. G.; Mountford, P. *Chem. Commun.* **2001**, 2738.

(29) Ta(NMe$_2$)$_5$ is also known to form imido ligands when reacted with primary amines, see: Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1978**, 579.

Table 2. Intermolecular Hydroamination of Various Alkynes with Aniline in the Presence of [V(μ^2-NPh)(NMe$_2$)$_2$]$_2$ (3) or [Ti(NPh)(NHPh)$_2$] (5)^a

Catalyst	Alkyne	Product Yield (%)^{b,c}	Selectivity (M:AM)^{d,e}	Alkyne Recovery (%)
3	Bu^n—≡—H	85	99:1	0
5		94	80:20	0
3	Ph—≡—H	48	99:1	0
5		80	97:3	0
3	Ph—≡—Ph	0	-	100
5		79	-	14
3	Ph—≡—Me	41	100:0^e	58
5		85	100:0^e	15
3	Et—≡—Et	5	-	93
5		15	-	82

^{a} Conditions: catalyst 0.2 mmol (except for the dimer 3: 0.1 mmol), alkyne 2 mmol, aniline 3 mmol, toluene 5 g, 100 °C (except for 1-hexyne, 80 °C), 24 h (except for 1-hexyne, 20 h with 3 and 4 h with 5). Unoptimized reaction and temperature conditions. ^{b} Compared with authentic samples, analyzed by GC-MS or ^{1}H NMR. ^{c} Yields were obtained by GC analysis vs dodecane internal standard. ^{d} Ratio Markovnikov to Anti-Markovnikov imine products by GC. ^{e} In the case of phenylpropyne hydroamination, the major product is an imine of benzylmethyl ketone.

As can be seen from Table 2 (with a comparison with 1-hexyne hydroamination at 80 °C), titanium complex **5** invariably gave better yields and faster rates than vanadium catalyst **3**. In addition, a common feature to both catalysts is the stronger difficulty to perform the hydroamination reactions while the steric hindrance increases on internal alkyne carbon atoms. As a result, using complex **5**, terminal alkynes such as 1-hexyne and phenylacetylene are hydroaminated faster than internal alkynes such as diphenylacetylene or 3-hexyne, and complex **3** is unable to perform the hydroamination of diphenylacetylene, bis(trimethylsilyl)acetylene, or 3-hexyne. Furthermore, the lower yields in the case of phenylacetylene hydroamination is due to side reactions that consume the alkyne substrate, giving oligomers of phenylacetylene or polyacetylene, as already evidenced with Ti-based catalyst **4**.[16a]

3. Hydroamination of 1-Hexyne with Various Amines.

Finally, we focused again on reactions with 1-hexyne. For that purpose, we performed hydroamination reactions at 80 °C in the presence of 10 mol % of catalyst **3** or **5** and employing various primary amines: aromatic amines with increasing steric hindrance at the 2,6-positions (PhNH$_2$, 2,6-Me$_2$-C$_6$H$_3$NH$_2$, 2,6-^{i}Pr$_2$-C$_6$H$_3$-NH$_2$), benzylic amine (PhCH$_2$NH$_2$), alkylamine (^{t}-BuNH$_2$), and a chiral amine ((S)-(−)-α-methylbenzylamine).

From the series of anilines, it is clear that steric hindrance of the amine plays a key role during the addition of the N−H bond to the carbon−carbon triple bond. As a result, the rates of 1-hexyne hydroamination are strongly reduced in both the Ti- and the V-catalyzed reaction when going from PhNH$_2$ to 2,6-^{i}Pr$_2$-C$_6$H$_3$NH$_2$. Meanwhile, the regioselectivity of the hydroamination reaction catalyzed by **5** is enhanced with hindered anilines (the selectivity of the reaction catalyzed by **3** being already very high with PhNH$_2$), with formation of almost exclusively the Markovnikov imine. Moreover, low yield of imines for the hydroamination of 1-hexyne with 2,6-Me$_2$-C$_6$H$_3$NH$_2$ or 2,6-^{i}Pr$_2$-C$_6$H$_3$NH$_2$ is also attributable to side reactions that consume the alkyne substrate. In particular, with **3** and to a lesser extent **5**, we observed products resulting from substrate oligomerization, in particular the cyclotrimerization of 1-hexyne leading to the two isomers (**A** and **B**) of tri-*n*-butylbenzene (**A** = 1,3,5-^{n}Bu$_3$-C$_6$H$_3$ and **B** = 1,3,4-^{n}Bu$_3$-C$_6$H$_3$ in a ratio **A:B** = ca. 60:40 with both catalysts, and 2,6-Me$_2$-C$_6$H$_3$NH$_2$ or 2,6-^{i}Pr$_2$-C$_6$H$_3$NH$_2$), a reaction already mentioned with Cp$_2$VMe$_2$ catalyst (vide supra). This side reaction is the main reaction when using the vanadium complex **3** with 2,6-^{i}Pr$_2$-C$_6$H$_3$NH$_2$, which consumes all the 1-hexyne introduced, but yields only 10% of imine product.

As complexes **3** and **5** possess an (=N−Ph) imido group, it is evident that during hydroamination of amines different from PhNH$_2$ there is also concomitant formation of a stoichiometric amount of the imine of PhNH$_2$. This problem can be overcome by using a catalyst having an imido group based on the amine used (and we have developed a general procedure to access these complexes[19b]).

When it comes to benzylamine hydroamination of 1-hexyne, unfortunately, both **3** and **5** are not effective catalysts under the conditions employed; low yields are obtained, with again formation of heavier byproducts.[30]

Interestingly, *tert*-butylamine hydroamination of 1-hexyne proceeded with moderate yield with titanium catalyst **5** (as opposed to Ti(NMe$_2$)$_4$, which does not catalyze ^{t}BuNH$_2$ hydroamination[16a]) and with a very good regioselectivity (M:AM 99:1), whereas vanadium complex **3** gave no reaction. Consequently, catalysis performed with **3** or **5** is in contrast with some other Ti-based catalysts[14a,15b] for which alkylamines give a better yield.
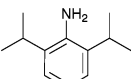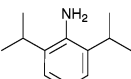
Finally, we tried the hydroamination of the chiral amine (S)-(−)-α-methylbenzylamine. Whereas **3** gave only low yield of imine products (10%),[31] catalyst **5** lead to the formation of 45% of imine products after 4 h at 80 °C.[32]

(30) In particular, the following organic compounds were identified by GC and GC−MS analyses: formation of the trimers **A** and **B** (when using catalyst **3**) and an unknown compound **C** (when using catalyst **5**) that was only identified by its molecular mass of 271, corresponding to two hexyne and one benzylamine fragment (this compound may result from a tandem reaction: dimerization of 1-hexyne leading to an enyne followed by its hydroamination).

(31) With **3**, two isomers of the imine are formed (ratio 3:7). We have not tried to fully identified the isomers and were unable to distinguish which isomer was the major one. We also noticed the formation of the trimers **A** and **B** among other side products.

(32) Three isomers are formed when using **5** (ratio 2:5:1, mass 203). Although we have not yet tried to fully characterized them, it is conceivable that these three isomers are the Markovnikov imine, the anti-Markovnikov imine, and an enamine product. Compounds **A**, **B**, and a compound **C**′ resulting from the condensation of two hexyne and one α-methylbenzylamine were also formed as side products (mass = 285).

Table 3. Intermolecular Hydroamination of 1-Hexyne with Various Primary Amines in the Presence of [V(μ^2-NPh)(NMe$_2$)$_2$]$_2$ (3) or [Ti(NPh)(NHPh)$_2$] (5)[a]

Catalyst	Alkyne	Time (h)[b]	Yield Imine (%)[c]	Selectivity (M:AM)[d]	Alkyne Recovery (%)
3	NH$_2$ (aniline)	20	85	99:1	0
5		4	94	80:20	0
3	NH$_2$ (2,6-dimethylaniline)	20	22	100:0	5
5		24	51	97:3	44
3	NH$_2$ (2,6-diisopropylaniline)	20	10	100:0	0
5		24	35	99:1	19
3	NH$_2$ (benzylamine)	24	<5	100:0	57
5		24	15	100:0	52
3	NH$_2$ (tert-butylamine)	20	0	-	95
5		4	59	99:1	5

[a] Conditions: catalyst 0.2 mmol (except for the dimer **3**: 0.1 mmol), 1-hexyne 2 mmol, amine 3 mmol (except for ᵗBuNH$_2$: 6 mmol), toluene 5 g, 80 °C. Reaction conditions are not optimized. [b] The reaction time has not been minimized. [c] Yields were obtained by GC analysis vs dodecane internal standard. [d] Ratio Markovnikov to Anti-Markovnikov imine products by GC.

On the basis of previous mechanistic studies on Ti precatalysts[17] supporting the hypothesis of a catalytically active metal imido intermediate, we propose a similar vanadium-imido species as the key intermediate in our vanadium hydroamination systems. This is supported by the fact that the hydroamination of a secondary amine (secondary amines cannot form an imido function) was not observed with our vanadium complexes **1**−**3**.

Conclusion

Screening of vanadium compounds toward alkyne hydroamination with primary amines has been conducted. Amido- or imido-vanadium(IV) complexes present an interesting catalytic activity for 1-hexyne hydroamination with aniline, with formation of almost exclusively the Markovnikov imine, although their activity is lower than that of Ti-based catalysts. A report has also been done on a tantalum(V) hydroamination precatalyst (Ta-(NMe$_2$)$_5$); it is the first time that group 5 (V(IV) and Ta-(V)) transition metal complexes are shown to be active alkyne hydroamination catalysts. Furthermore, a new imido-Ti(IV) catalyst has been prepared and is an efficient catalyst giving good regioselectivity in Markovnikov imine. All these systems have been found to be competent catalysts for the intermolecular addition of sterically less demanding arylamines to preferably terminal alkynes. In the V system, we expect that further studies will confirm the hypothesis of an imido species as the key intermediate. Work is also in progress to further develop and optimize these systems.

Experimental Section

General Remarks. All syntheses were carried out under argon using standard Schlenk line or drybox techniques and predried glassware. All hydroamination reactions and complex synthesis were performed in an argon-filled Vacuum Atmospheres inert atmosphere box. Solvents were refluxed and dried over appropriate drying agents under an atmosphere of argon, collected by distillation, and stored in the drybox over 4 Å molecular sieves. Alkyne or amine substrates were dried over appropriate drying agent before use. Ti(NMe$_2$)$_4$ (Aldrich) was used as received. V(NMe$_2$)$_4$, [V(μ^2-NPh)(NMe$_2$)$_2$]$_2$, [V(NEt$_2$)$_2$-(THF)$_4$][B(C$_6$F$_5$)$_4$]$_2$, and V(NSiMe$_3$)$_2$)$_3$ were prepared according to known procedures.[19b,33−35] NMR solvents were sparged with argon and stored over 4 Å molecular sieves in a drybox. NMR data were recorded using AMX-400, DPX-300, or AC-250 MHz Bruker spectrometers and referenced internally to residual protonated-solvent (^{1}H) resonances and are reported relative to tetramethylsilane ($\delta = 0$ ppm). EPR spectra were recorded on a Bruker ESP300E spectrometer. Infrared spectra were prepared as KBr pellets under argon in a glovebox and were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrometer. Infrared data are quoted in wavenumbers (cm^{-1}). Elemental analyses and GC−MS analyses were performed at the Laboratoire de Chimie de Coordination (Toulouse, France). GC analyses were recorded using a Shimadzu GC-14B gas chromatograph equipped with a HP5 (15 m × 0.530 mm × 1.5 μm) column or a Hewlett-Packard HP4890A gas chromatograph equipped with a 25QC5/BP624 or HP-5 (25 m × 0.530 mm × 1.5 μm) column.

Synthesis of V(carb)$_2$(NMe$_2$)$_2$ (2). To a green solution of V(NMe$_2$)$_4$ (250 mg, 1.10 mmol) was added 368 mg of carbazole (2.20 mmol) by portions, at room temperature under stirring. After 1 h, dimethylamine formed was quickly removed by connecting to the vacuum and the solution was stirred overnight. To this brown solution was carefully layered pentane, resulting in the formation of red crystals of **2** (477 mg, 92%). EPR (toluene, 20 °C): $g = 1.980$, $a(^{51}V) = 69$ G. μ_{eff}(20 °C) = 1.80 μ_B. Anal. Calcd for C$_{28}$H$_{28}$N$_4$V: C, 71.33; H, 5.99; N, 11.88. Found: C, 70.29; H, 5.75; N, 11.56.

Synthesis of [Ti(NPh)(NHPh)$_2$] (5). A 498 mg portion of aniline (5.352 mmol) was added dropwise to a toluene solution (5 mL) of 400 mg of Ti(NMe$_2$)$_4$ (1.784 mmol). The resulting red solution was stirred at 110 °C overnight. The red microcrystalline solid was separated by decantation, washed with toluene (2 × 10 mL) and pentane (3 × 10 mL), and dried under vacuum. Yield: 405 mg (70%). IR: 3263 (w, NH), 2917 (w), 1577 (m, C=C), 1473 (s), 1255 (vs), 1067 (m), 1024 (m), 889 (m), 753 (s), 690 (s), 552 (m), 498 (m). Anal. Calcd for C$_{18}$H$_{17}$N$_3$-Ti: C, 66.89; H, 5.30; N, 13.00. Found: C, 66.64; H, 5.12; N, 13.20. The strong insolubility of **5** precluded any NMR investigation (**5** is insoluble in toluene, pentane, acetonitrile, THF, or pyridine and reacts with dichloromethane), suggesting that **5** might be an oligomeric material of the type [Ti(NPh)-(NHPh)$_2$]$_n$. By hydrolysis of **5**, only the formation of aniline was observed (by ^{1}H NMR and MS). Reaction of **5** with ketones: 1.1 equiv of ketone ((CD$_3$)$_2$C=O or Ph$_2$C=O) (0.03403 mM) was added to a solution containing 10 mg of **5** (0.03094 mM) dissolved in 1.00 g of toluene. Upon mixing (at RT for 6 h, (CD$_3$)$_2$CO, or at 80 °C for 10 h, Ph$_2$CO) ,a white precipitate (presumably oligomeric titanium oxide) formed. The imines ((CD$_3$)$_2$C=NPh and Ph$_2$C=NPh) were identified by GC and GC−MS (MS(IC): m/z 139 for (CD$_3$)$_2$CNPh and 257 for Ph$_2$-CNPh).

Typical Procedure for the Hydroamination Reaction (Tables 1−3). All manipulations of the solutions were done in the glovebox under an atmosphere of argon. In a screw cap flask was loaded 0.2 mmol of the catalyst, amine (3 mmol), dodecane (1 mmol), and alkyne (2 mmol) and diluted with 5.00 g of toluene. The flask was heated with stirring at 80 °C (temperature of the oil bath). The reaction mixture was analyzed

Table 4. Crystal Data and Structure Refinement Parameters for 2 and 3

	2	3
chemical formula	$C_{28}H_{28}N_4V$	$C_{10}H_{17}N_3V$
fw	470.94	230.21
cryst syst	monoclinic	monoclinic
space group	$P2_1$	$P2_1/c$
a, Å	9.8271(12)	8.4907(18)
b, Å	13.3200(13)	10.816(3)
c, Å	18.497(3)	13.500(3)
α, deg	90.0	90.0
β, deg	100.183(18)	106.93(2)
γ, deg	90.0	90.0
V, Å^3	2383.0(5)	1186.1(5)
Z	4	4
D_{calc}, g cm^{-3}	1.168	1.289
μ(Mo Kα), mm^{-1}	0.431	0.804
$F(000)$	876	484
θ range (deg)	1.6 to 26.1	3.1 to 21.9
no. of measd reflns	10 423	5588
no. of unique reflns/R_{int}	4941/0.1076	1447/0.0811
no. of params/restraints	1423/606	173/0
final R indices $[I > \sigma2(I)]$	$R_1 = 0.1015$, $wR_2 = 0.2621$	$R_1 = 0.0649$, $wR_2 = 0.0713$
final R indices all data	$R_1 = 0.1382$, $wR_2 = 0.2932$	$R_1 = 0.1126$, $wR_2 = 0.0823$
goodness of fit	1.145	1.141
$\Delta\rho_{max} - \Delta\rho_{min}$, e·Å^3	0.536 and -0.843	0.409 and -0.253

by GC versus dodecane internal standard. Note: Although the reaction was carried out at 80 °C, hydroamination of 1-hexyne with aniline usually exhibits formation of imine products a few minutes after mixing at room temperature.

Crystal Structure Determination of 2 and 3. For the four compounds data were collected at low temperature ($T = 180$ K) on a Stoe imaging plate diffraction system (IPDS), equipped with an Oxford Cryosystems cryostream cooler device and using a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Final unit cell parameters were obtained by means of a least-squares refinement of a set of 8000 well-measured reflections, and the crystal decay was monitored during data collection by measuring 200 reflections by image; no significant

fluctuation of intensities has been observed. Structures have been solved by means of direct methods with the program SIR92.[36] Subsequent difference Fourier maps and models were refined by least-squares procedures on F^2 by using SHELXL-97[37] integrated in the package WINGX version 1.64,[38] and empirical absorption corrections were applied to the data.[39] All hydrogen atoms have been located on difference Fourier maps and introduced in the refinement as fixed contributors using a riding model with an isotropic thermal parameter fixed at 20% higher than those of the C sp^2 atoms and 50% for the C sp^3 atoms to which they were connected. Concerning the methyls groups they were refined with the torsion angle as a free variable. All non-hydrogen atoms were anisotropically refined, and in the last cycles of refinement weighting schemes have been used, where weights are calculated from the following formula: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

Supporting Information Available: Tables of atomic coordinates and bond distances and angles for complexes **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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