Journal of Organometallic Chemistry 696 (2011) 235–243

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

# Understanding the role of an easy-to-prepare aldimine–alkyne carboamination catalyst, $[Ti(NMe_2)_3(NHMe_2)][B(C_6F_5)_4]$

Falguni Basuli, Benjamin Wicker, John C. Huffman, Daniel J. Mindiola*

*Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, IN 47405, USA*

ARTICLE INFO

*Article history:*
Received 4 August 2010
Received in revised form
2 September 2010
Accepted 3 September 2010
Available online 21 September 2010

*Keywords:*
Carboamination
Titanium
Imido
Nitrogen

ABSTRACT

A series of reactivity studies of the carboamination pre-catalyst $[Ti(NMe_2)_3(NHMe_2)][B(C_6F_5)_4]$ as well as the preparation of other catalysts are reported in this work. Treatment of $[Ti(NMe_2)_3(NHMe_2)][B(C_6F_5)_4]$ with the aldimines Ar′N=CHtol (Ar′ = 2,6-$Me_2C_6H_3$, tol = 4-$MeC_6H_4$), and depending on the reaction conditions, results in isolation of $[Me_2N{=}CHR'][B(C_6F_5)_4]$ (**1**) or $(Me_2N)_2$CHtol, as well as the asymmetric titanium dimer $[(Me_2N)_2(HNMe_2)Ti(\mu_2\text{-}N[2,6\text{-}Me_2C_6H_3])_2Ti(NHMe_2)(NMe_2)][B(C_6F_5)_4]$ (**2**). Protonation of $CpTi(NMe_2)_3$ and $Cp^*Ti(NMe_2)_3$ results in isolation of the salts, $[CpTi(NMe_2)_2(NHMe_2)][B(C_6F_5)_4]$ (**3**) and $[Cp^*Ti(NMe_2)_2(NHMe_2)][B(C_6F_5)_4]$ (**4**), respectively. Treatment of compounds **3** or **4** with $H_2N[2,6\text{-}{}^iPr_2C_6H_3]$ results in formation of the imido salts $[CpTi({=}N[2,6\text{-}{}^iPr_2C_6H_3])(NHMe_2)_2][B(C_6F_5)_4]$ (**5**) (58% yield) or $[Cp^*Ti({=}N[2,6\text{-}{}^iPr_2C_6H_3])(NHMe_2)_2][B(C_6F_5)_4]$ (**6**). When $Ti(NMe_2)_4$ is treated with $[Et_3Si][B(C_6F_5)_4]$, the salt $[Ti(NMe_2)_3(N[SiEt_3]Me_2)][B(C_6F_5)_4]$ (**7**) is obtained, and treatment of the latter with $[2,6\text{-}{}^iPr_2C_6H_3]N{=}$CHtol produces the imine adduct $[Ti(NMe_2)_3(\kappa^1\text{-}[2,6\text{-}{}^iPr_2C_6H_3]N{=}CHtol)][B(C_6F_5)_4]$ (**8**). The carboamination catalytic activity of complexes **2**–**7** was investigated and compared to $[Ti(NMe_2)_3(NHMe_2)][B(C_6F_5)_4]$. Likewise, a proposed mechanism to the active carboamination catalyst stemming from $[Ti(NMe_2)_3(NHMe_2)][B(C_6F_5)_4]$ is described.

## 1. Introduction

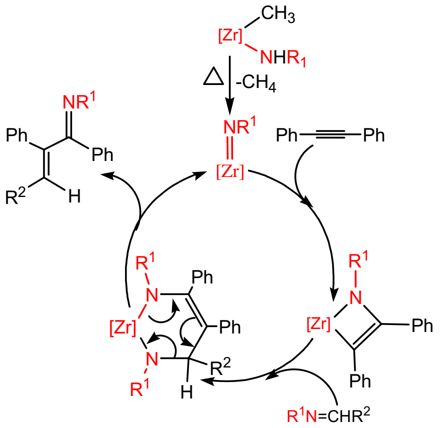
In 2004 the Bergman group discovered a catalytic reaction where an aldimine can be added across an internal alkyne to form an α,β-unsaturated imine (denoted as the carboamination of alkynes with aldimines, Scheme 1) [1,2]. This interesting transformation was made possible via the use of a transient, mononuclear zirconocene imido precursor, $[Cp_2Zr{=}NAr]$ (Ar = *p*-substituted aryl where the *p*-group is H, OMe, or Me), which could reversibly [2 + 2]-cycloadd the alkyne, then insert the aldimine into the Zr–C bond of the azametallacyclobutene species (Scheme 1) [1,2]. A [4 + 2] retrocycloaddition stemming from the six-membered metallacycle resulted in extrusion of α,β-unsaturated imine concurrent with regeneration of the imido thereby closing the cycle for carboamination of alkynes with aldimines (Scheme 1). Cleverly, the Bergman system applied a zirconium pre-catalyst $Cp_2Zr(NHAr)(CH_3)$ (or the corresponding metallacyclobutene complex resulting from [2 + 2]-cycloaddition of the alkyne across the Zr=N bond of $[Cp_2Zr{=}NAr]$), which underwent thermolytic α-hydrogen abstraction to generate the transient imide, $[Cp_2Zr{=}NAr]$. In the absence of the alkyne such an intermediate would dimerize thereby killing its catalytic activity. Despite this attractive entry to these new organic frameworks, typical reaction conditions involving the metallocene system required extensive time frames, high temperatures using 10–20 mol% of catalyst, as well as the system had also limited range of functional group tolerance at both the aldimine and alkyne substrates [2]. The reaction also suffered from not being atom-economical when the imido group on zirconium was inequivalent to the aldimine *N*-aryl group given the ability of $[Cp_2Zr{=}NAr]$ to undergo imine metathesis with the aldimine and hence afford a mixture of α,β-unsaturated imines when $R^2 \neq R^1$ (Scheme 1) [3]. This was the consequence of having a mixture of $[Cp_2Zr{=}NAr]$ catalysts which would unavoidably result in two separate cycles therefore lowering the yield of the unsaturated organic product.

In an attempt to circumvent some of these limitations, and given our interest in the reactivity and the catalytic ability of 3d early-transition metal complexes having metal-ligand multiple bonds [4,5], we explored the role of various titanium imidos [6–9] in this interesting reaction given the fact that N–C and C–C bonds are catalytically formed and broken. In this contribution we report some investigations toward understanding the role of an easy-to-prepare carboamination pre-catalyst, $[Ti(NMe_2)_3(NHMe_2)][B(C_6F_5)_4]$ [9], by examining the source and role of the imide, variance of the dimethylamide ancillary ligand, and anion or activator being used in the catalytic process.

---

* Corresponding author. Fax: +1 812 855 8300.
*E-mail address:* mindiola@indiana.edu (D.J. Mindiola).

0022-328X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2010.09.017



**Scheme 1.** Proposed Carboamination Cycle Using a Zirconium-Imide Precursor [Zr] = $Cp_2Zr$.

## 2. Results and discussion

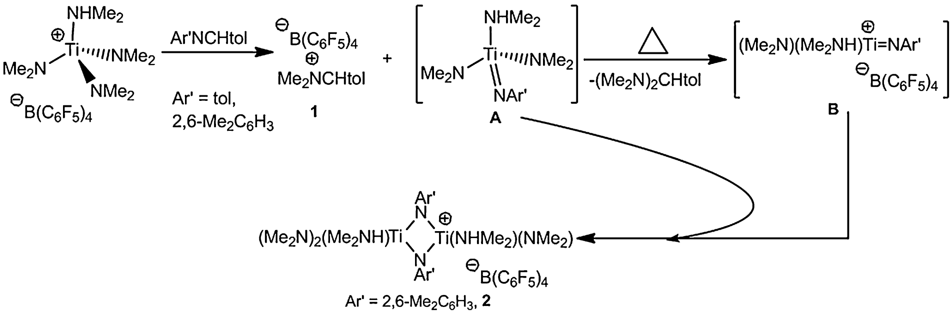
### 2.1. Understanding the source of the imide using the carboamination pre-catalyst [$Ti(NMe_2)_3(NHMe_2)$][$B(C_6F_5)_4$]

We reported previously that mixing of the commercially available reagents $Ti(NMe_2)_4$ with [$NHMe_2Ph$][$B(C_6F_5)_4$] gives rise to the salt, [$Ti(NMe_2)_3(NHMe_2)$][$B(C_6F_5)_4$], which has been demonstrated to be a very reactive pre-catalyst for the carboamination of alkynes with aldimines [9]. It was found that neither the anilinium proton source nor the neutral titanium complex, alone, were active catalysts for this transformation, which was surprising given that $Ti(NMe_2)_4$ has been shown by Odom and Schafer to be a highly active hydroamination catalyst [10–12]. One peculiar feature of this reaction that we found intriguing was the source of the imide ligand during the carboamination process. It was determined that the absence of aniline, which was presumed to be the source of imido, had no effect in the catalytic formation of the α,β-unsaturated imine [9]. This was puzzling since it is generally accepted that a terminal imido ligand is being transferred in the catalytic cycle (Scheme 1, vide supra) [4,13,14]. The fact that a catalytic carboamination process could occur in the absence of aniline suggested that the imide group is derived from the aldimine as opposed to the aniline. Therefore, we investigated another mechanism to formation of the imide which did not involve the more common route, such as transimination (imide formation derived from aniline deprotonation) [4].

It has been reported that aldimines can serve as an imido source in the presence of suitable nucleophiles [15]. Accordingly, we explored the reactivity of [$Ti(NMe_2)_3(NHMe_2)$][$B(C_6F_5)_4$] with aldimines such as Ar′N=CHtol (Ar′ = 2,6-$Me_2C_6H_3$, tol = 4-$MeC_6H_4$) (Scheme 2) in the absence of diphenylacetylene. Although the reaction yielded a mixture of products after 3 days at 25 °C, we were able to isolate, in low yield, the iminium salt, [$Me_2N$=CHR′][$B(C_6F_5)_4$] (**1**) (Scheme 2). A single crystal X-ray structure, NMR spectroscopic data and combustion analysis confirmed the proposed connectivity of **1** (Fig. 1)-see Supplementary material. This result therefore suggested that the “NAr” motif of the imine serves as the imido source via the substitution of one $-NMe_2$ ligand in [$Ti(NMe_2)_3(NHMe_2)$][$B(C_6F_5)_4$]. The most notable structural feature of **1** (Fig. 1) is formation of an iminium motif (N=C, 1.307(6) Å versus N–C bonds of 1.466(5) and 1.470(6) Å), consequently resulting in formation of a planar nitrogen (sum of C–N–C angles = 360°). The reaction depicted in Scheme 2 implies that a neutral, four-coordinate titanium imido, [ArN=$Ti(NMe_2)_2(NHMe_2)$] (**A**), is likely generated in the reaction mixture along with other side products (Scheme 2), although we have no spectroscopic evidence for formation of **A** given the complexity of the mixture. Likewise, attempted synthesis of putative **A** from reactions such as $Ti(NMe_2)_4$ and various anilines failed to produce any isolable product(s) given the lipophilic nature of the complexes being formed.

We, however, argue against **A** being the active catalyst in the carboamination cycle since $Ti(NMe_2)_4$ fails to catalyze the carboamination of alkynes with aldimines in the presence or absence of aniline [9]. Therefore, we propose compound **1** and putative **A** to be formed early in the reaction, but then react to form what we speculate to be the active form of the catalyst. Our hypothesis is in part, corroborated by an independent reaction using similar conditions to those of the catalytic reaction (thermolyzing the mixture). Accordingly, treating tolN=CHtol or [2,6-$Me_2C_6H_3$]N=CHtol with 1 eq. of [$Ti(NMe_2)_3(NHMe_2)$][$B(C_6F_5)_4$] in the absence of the alkyne, and then heating the mixture for 5 days at 25 °C afforded a mixture of products from which the organic side product, $(Me_2N)_2$CHtol could be observed by $^1H$ NMR spectroscopy and MS analysis as well as comparison with an independently prepared sample [16]. Although we were unable to characterize any titanium products from the reaction involving tolN=CHtol and [$Ti(NMe_2)_3(NHMe_2)$][$B(C_6F_5)_4$], the use of a more hindered aldimine, [2,6-$Me_2C_6H_3$]N=CHtol, allowed for isolation of one titanium product. In this case, small quantities of a titanium complex were obtained by fractional crystallization of the reaction mixture from a solution of $C_6H_5F$ layered with hexane. The $^1H$ NMR spectrum of these crystals revealed formation of an asymmetric complex due to the observation of broad and inequivalent $-NMe_2$ and $-NHMe_2$ resonances. Single crystal structural analysis confirmed this compound to be the imido titanium dimer, [$(Me_2N)_2(HNMe_2)Ti(\mu_2$-N[2,6-$Me_2C_6H_3$]$)_2Ti(NHMe_2)(NMe_2)$][$B(C_6F_5)_4$] (**2**) (Fig. 2)-see Supplementary material.

The molecular structure of **2** displays several interesting features such as formation of an asymmetric $Ti_2N_2$ core (Ti1–N3, 1.800(3); Ti1–N12, 1.877(3); N3–Ti1–N12, 92.93(12); N3–Ti2–N12, 78.49(10); Ti1–N3–Ti2, 92.60(11); Ti1–N12–Ti2, 95.77(11)) due to the bridging of two imido ligands to inequivalent metal centers. These imide groups are most likely derived from the aldimine [2,6-$Me_2C_6H_3$]N=CHtol. As



**Scheme 2.** Proposed route to formation of compound **1** and the titanium complex **2**.