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Snapshots of an Alkylidyne for Nitride Triple-Bond Metathesis

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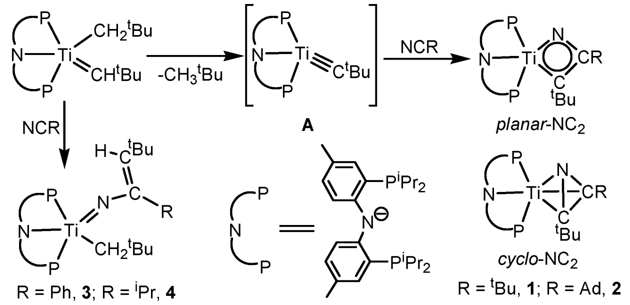
Metathesis reactions involving alkynes and M≡CR linkages constitute an important and an emerging field from a stoichiometric and catalytic perspective.[1,2] Moreover, the process denoted “alkyne metathesis” is now becoming a standard procedure for reactions such as cross-metathesis[3,4] and ring-closing metathesis,[2] the latter of which has resulted in the design of natural products, and pharmaceutically important molecules.[2] Although alkyne metathesis or Wittig-like reactions are a known occurrence in organotransition metal chemistry[1−4] and metal−metal multiply bonded frameworks,[5] metathetical reactions involving alkylidynes in groups 4 or 5 have thus far been unknown.[1,3k] This situation may be traced to the scant number of terminal transition metal alkylidyne systems prior to group 6.[1,6]

Given our ability to generate highly nucleophilic and terminal titanium alkylidynes,[7] it was speculated that nitriles should undergo alkylidyne for nitride exchange. This hypothesis was particularly appealing for two reasons. Azametallacyclobutadiene intermediates along the alkylidyne/nitrile metathesis, involving M≡CR linkages, have been proposed but not observed.[3c,i,j] Additionally, terminal titanium nitrides (or group 4 nitrides) are an unknown class of ligands and are expected to be inherently reactive given the likely polarized nature of the M≡N multiple bond.

In this paper we show that nitriles, such as N≡C^{t}Bu and N≡CAd (Ad = 1-adamantyl), [2+2] cycloadd across the neopentylidyne linkage of intermediate (PNP)Ti≡C^{t}Bu[7] (**A**) (PNP = *N*[2-P(CHMe$_2$)$_2$-4-methylphenyl]$_2^-$), to afford the first examples of azametallacyclobutadienes, specifically (PNP)Ti(NCRC^{t}Bu) (R = ^{t}Bu, **1**; Ad, **2**). Addition of electrophiles such as Me$_3$SiCl or Al(CH$_3$)$_3$ to the latter complexes promote complete ^{t}BuC^{3-} for N^{3-} exchange thus forming the trapped titanium nitride concurrent with extrusion of the alkyne ^{t}BuC≡CR. A combination of computational and isotopic labeling studies support the notion that the metallacycle scaffolds in **1** and **2** are planar rings, with significant multiple bond character between Ti and N. In addition, experiments utilizing ^{15}N enriched ^{15}N≡CAd[4,8] clearly reveal the titanium imide nitrogen to originate from complete metathetical exchange with the nitrile.

When (PNP)Ti═CH^{t}Bu(CH$_2$^{t}Bu)[7] is treated with N≡C^{t}Bu (neat or stoichiometric), immediate precipitation of an orange colored solid, **1**, is readily observed (Scheme 1). In C$_6$D$_6$, the ^{1}H NMR spectrum of **1** is indicative of formation of a single titanium product having two inequivalent ^{t}Bu groups, as well as an asymmetric PNP framework. The latter salient feature is further manifested by two doublets in the ^{31}P NMR spectrum. Most notably, the ^{13}C NMR spectrum of **1** revealed two highly deshielded resonances at 240.5 and 178.0 ppm, neither of which is coupled to a H, and is comparable to ^{13}C resonances for previously reported tungstenacyclobutadienes.[9] When an analogous reaction involving (PNP)-Ti═CH^{t}Bu(CH$_2$^{t}Bu) and N≡CAd is conducted in C$_6$H$_{12}$, complex **2** also precipitates as an orange colored powder in high yield (73%, Scheme 1). Multinuclear NMR spectral data for **2** displays similar spectroscopic signatures to **1**.[8,9] When the reaction was performed in cyclohexane using a slight excess of ∼40% enriched ^{15}N≡CAd,[4,8] the ^{15}N NMR spectrum of (PNP)Ti(^{15}NCAdC^{t}Bu) (**2**)-**^{15}N** signified a deshielded resonance at 672.6 ppm (55 °C, referenced to NH$_3$(l) at 0 ppm).[8] On the basis of the above observations, we propose that transient **A** undergoes a [2+2] cycloaddition of N≡CR to afford the azatitanacyclobutadiene species (*planar*-NC$_2$), **1** and **2** (Scheme 1).[9] However, given our inability to obtain suitable crystals for X-ray diffraction analysis, it is possible to propose that the NC$_2$ fragment in systems such as **1** and **2** could also be bonded as an η^3-azacyclopropyltrianyl (*cyclo*-NC$_2$, Scheme 1). Despite this possibility, the highly deshielded ^{15}N resonance for the NC$_2$ framework in **2-^{15}N** agrees well with our predicted ^{15}N NMR chemical shift by DFT methods (675.8 ppm),[8] thus suggesting that **1** and **2** contain planar TiNC$_2$ motifs with significant Ti−N multiple bond character. In addition, computational studies predict the *cyclo*-NC$_2$ isomer of **1** to be 39.6 kcal/mol higher in electronic energy (E(SCF)) versus the planar TiNC$_2$ surrogate, and the ^{15}N NMR chemical shift for this geometry is located 361.4 ppm upfield from the experimental value (vide supra).[8]

Scheme 1. [2+2] Cycloaddition Reactions with Nitriles Involving Both Ti≡C^{t}Bu and Ti═CH^{t}Bu Linkages



Formation of **1** and **2** is highly dependent on the nature of the nitrile. Consequently, when less hindered nitriles such as N≡CR (R = Ph, ^{i}Pr) are employed, Wittig-like chemistry precedes α-hydrogen abstraction, thus taking place exclusively at the alkylidene moiety in (PNP)Ti═CH^{t}Bu(CH$_2$^{t}Bu) to afford the imide-alkyls (PNP)Ti═N[C(R)CH^{t}Bu](CH$_2$^{t}Bu) (R = Ph, **3**; R = ^{i}Pr, **4**) in excellent yields (Scheme 1).[8] In addition to multinuclear NMR spectroscopic characterization (**3** and **4**), compound **3** has been scrutinized by single-crystal X-ray diffraction.[8]

Despite the TiNC$_2$ ring in complexes **1** and **2** being antiaromatic, they are exceedingly stable up to 100 °C when excluded from moisture and air. No exchange was observed when **1** or **2** was heated in an excess of NC^{t}Bu, NCAd, PhC≡CPh, or (CH$_3$)$_3$SiC≡CSi(CH$_3$)$_3$ thus hinting that the azatitanacyclobutadiene core in **1** and **2** is not amenable to fragmentation under these conditions. However, when complexes **1** and **2** were treated with ClSi(CH$_3$)$_3$,

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10.1021/ja0689684 CCC: $37.00

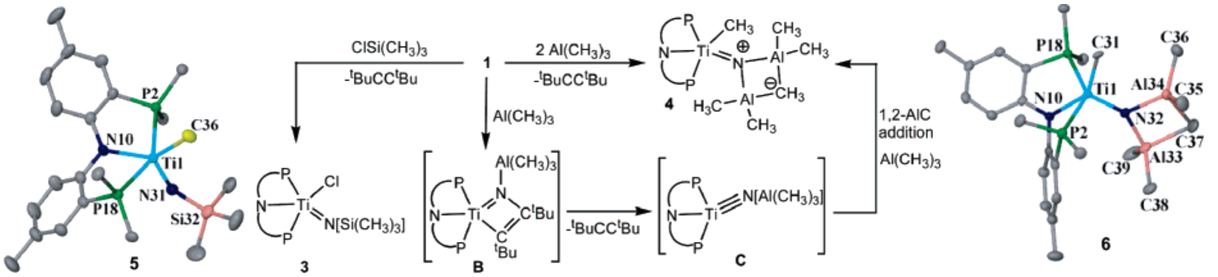

Figure 1. Synthesis of **5** and **6** and molecular structures with H-atoms, solvent, independent molecules, and isopropyl methyls excluded for clarity.

complete ${}^{t}BuC^{3-}$ for N^{3-} exchange occurred quantitatively, concurrent with extrusion of the alkyne $RC{\equiv}C^{t}Bu$ ($R = {}^{t}Bu$ and Ad) and formation of the trimethylsilyl imide complex $(PNP)Ti{=}N[Si(CH_3)_3](Cl)$ (**5**) (Figure 2).[8] The former organic byproduct was confirmed via ^{1}H and ^{13}C NMR spectra, while the identity of complex **5** was established by an independent synthesis.[10] In addition, the X-ray structure of **5** has been determined and unarguably depicts a five-coordinate titanium complex bearing a bent terminal trimethylsilyl imide functionality (Ti═N, 1.709(9) Å; Ti═N−Si, 151.9(2); Figure 1). The imide nitrogen in **5** was unequivocally confirmed to originate from nitrile metathesis with the transient $Ti{\equiv}C^{t}Bu$ ligand, since the isotopomer **2-^{15}N** cleanly produced $(PNP)Ti{=}^{15}N[Si(CH_3)_3](Cl)$ (**5**)**-^{15}N** (^{15}N NMR: 553.9 ppm, $J_{NP} = 2.3$ Hz) when treated with $ClSi(CH_3)_3$.[8]

When **1** or **2** was exposed to an excess of $Al(CH_3)_3$, ${}^{t}BuC{\equiv}CR$ was also formed along with the imide zwitterion $(PNP)Ti{=}N[Al_2(CH_3)_4(\mu\text{-}CH_3)](CH_3)$ (**6**).[8] Salient ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic features for **6** reveal a system bearing an intact PNP framework, and fluxional $Al_2(CH_3)_4(\mu\text{-}CH_3)$ motif.[8] However, the ^{27}Al NMR spectrum of **6** evinced two broad Al resonances at 54 and 141 ppm in an 80:20 ratio, respectively.[8] This feature was further corroborated by the ^{15}N NMR spectrum of the ^{15}N isotopically enriched $(PNP)Ti{=}^{15}N[Al_2(CH_3)_4(\mu\text{-}CH_3)](CH_3)$ (**6**)**-^{15}N**, prepared from **2-^{15}N** and 2 equiv of $Al(CH_3)_3$, which also displayed two independent resonances at 527.9 (major) and 563.6 (minor) ppm.[8] As a result, the ^{27}Al and ^{15}N NMR solution spectra suggests at least two Ti species being present in solution.

To conclusively elucidate the connectivity of compound **6**, a single-crystal structural analysis was conducted. Amid the many salient features, the molecular structure clearly exposes a zwitterionic titanium imide-methyl complex (Ti-N32, 1.758(9); Ti-C31, 2.154(3) Å; Figure 1), bearing both an $^{+}Al(CH_3)_2$ and an $Al(CH_3)_3$ at the imide nitrogen.[8] Therefore, each $Al(CH_3)_2$ fragment shares a $^{-}CH_3$ group by virtue of a $3c{-}2e^{-}$ bond. The imaginary plane composing the planar NAl_2C fragment bisects the PNP framework, and Ti═N multiple bond formation in **6** is evident when the short distance of 1.758(9) Å is compared to the pincer Ti−N amide linkage (2.038(8) Å). Consequently, the latter feature renders the former atom planar. The solid-state structure of **6** appears to be the lowest energy geometry and may not be reflective of how this system behaves in solution at room temperature.

Formation of compounds **5** and **6** raises the question as to whether a transient titanium nitride is generated during the course of the reaction. While complex **5** is unarguably formed via a putative trimethylsilyl cation adding to the azatitanacyclobutadiene nitrogen in **1** or **2**, formation of **6** obviously occurs by a different pathway. As depicted in Figure 1, $Al(CH_3)_3$ likely coordinates to the azametallacyclobutadiene nitrogen in **1** or **2** to afford transient **B**, which ultimately ejects the alkyne ${}^{t}BuC{\equiv}CR$ to form the Lewis acid stabilized nitride **C**. By manner of a 1,2-AlC bond addition across the reactive Ti≡N linkage, and subsequent binding of another $Al(CH_3)_3$, formation of **6** is then plausible. However, we are unsure as to whether 1,2-AlC bond addition occurs prior to or after binding of the second $Al(CH_3)_3$.

Acknowledgment. We thank Indiana University-Bloomington, the Dreyfus Foundation, the Sloan Foundation, and the NSF (Grant CHE-0348941 to D.J.M.) for financial support of this research and John J. Curly for insightful discussions.

Supporting Information Available: All experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0689684