ORGANOMETALLICS

pubs.acs.org/Organometallics Article

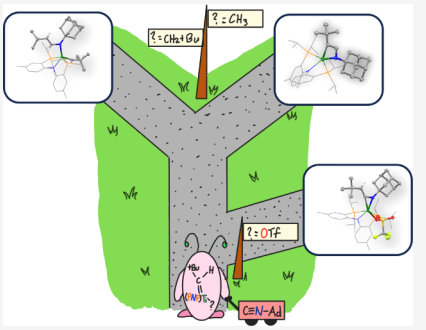
Isonitrile Insertion into Titanium Neopentylidene Alkyl Complexes Yields a Bifurcated Pathway to Form κ^1-*N*-vinylamido or κ^2-*C*,*N*-azaalleneyl Fragments

John B. Russell, Michael R. Gau, Patrick J. Carroll, and Daniel J. Mindiola*

Cite This: *Organometallics* 2025, 44, 279−288 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

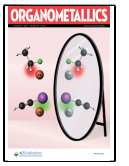
ABSTRACT: Three organometallic ligand scaffolds resulting from the insertion of 1-adamantyl isonitrile (C≡NAd; Ad = $C_{10}H_{15}$) into titanium neopentylidene complexes, [(PNP)Ti=CH^{t}Bu(X)] are described herein. Treatment of the titanium neopentylidene complex (PNP)Ti=CH^{t}Bu(OTf) (**1**-OTf, PNP$^-$ = N[2-P^{i}Pr$_2$-4-methylphenyl]$_2^-$, OTf = trifluoromethanesulfonate$^-$) with one equivalent of C≡NAd leads to the formation of a titanium η^2-*C*,*N*-ketenimine, (PNP)Ti(η^2-*C*,*N*-Ad**NC**CH^{t}Bu)(OTf) (**2**-OTf). However, when the titanium neopentylidene neopentyl complex (PNP)Ti=CH^{t}Bu(CH$_2^t$Bu) (**1**-Np) is added one equivalent of C≡NAd, a titanium neopentylidene κ^1-*N*-vinylamido complex (PNP)Ti=CH^{t}Bu(κ^1-*N*-Ad**N**CHCH^{t}Bu) (**3**) is formed. In contrast, the titanium neopentylidene methyl complex (PNP)Ti=CH^{t}Bu(CH$_3$) (**1**-Me) reacts with one equivalent of C≡NAd to produce a rare chelating κ^2-*C*,*N*-azaalleneyl ligand, in the complex (PNP)Ti(κ^2-*C*,*N*-Ad**NC**C^{t}Bu) (**4**), with concurrent extrusion of methane. Independently, it is shown that treatment of **2**-OTf with one equivalent of neopentyl lithium (LiNp, Np$^-$ = CH$_2^t$Bu) or a half equivalent of dimethyl magnesium (MgMe$_2$) smoothly forms complex **3** or **4**, respectively, and suggests that the η^2-*C*,*N*-ketenimine ligand in **2**-OTf might be an intermediate ligand enroute to the neopentylidene κ^1-*N*-vinylamido or κ^2-*C*,*N*-azaalleneyl complexes. Complexes **2**-OTf, **3** and **4** have been structurally and spectroscopically characterized and a proposed mechanism for the formation of complexes **3** and **4** is also described.



INTRODUCTION

Complexes containing metal−carbon multiple bonds (MCMBs) have exhibited a diverse array of reactivity due to the highly polarized nature of the bond and the ability of these systems to promote the exchange of carbene or carbyne units. This strategy has resulted in the development of the mature fields of alkene metathesis,[1−5] and alkyne metathesis,[6−12] and more recently, the burgeoning field of cyclic conjugated polymer catalysis.[13−35] In addition to metathesis and polymer chemistry, complexes containing MCMBs can be used for developing new synthetic building blocks for furnishing carbocyclic[36−46] and *N*-based heterocyclic four,[47,48] five,[43,47,49−54] and even six−membered rings[55] among other organic archetypes.[47,56−65] One plausible pathway to access complexes of this type, as well as unsaturated organic fragments, involves the insertion of an isonitrile (C≡NR) into MCMBs. This strategy allows access to metal bound ketenimines (Figure 1, left) which are the key to furnishing the new synthetic building blocks,[66] including the formation of free ketenimine species.[67,68] To the best of our knowledge, the insertion of C≡NR into MCMBs can be traced as far back as studies by Fischer and Aumann.[69] In their report, the authors showed that insertion of C≡NR into Fischer-type carbenes could lead to the formation of metal ketenimine complexes, with the organic scaffold being bound κ^1 through the N position, κ^1-*N*- (Figure 1C). Subsequent reports of Fischer and Schrock carbenes and carbynes have demonstrated that the metal ketenimine ligands can be construed in a variety of ways and that these scaffolds are versatile and have many isomeric binding modes to metal ions. These coordination modes for ketenimine ligands binding to metal ions include; (η^2-*C*,*N*-),[70−75] (η^2-*C*,*C*-),[76−78] (κ^1-*N*-),[69,75,79,80] (σ^1-*N*-),[69] (σ^1-*C*-),[81] and (σ^1-*O*-),[82] which are illustrated in Figure 1A−F, respectively. Recent studies by Cadierno, Gimeno et al.[83,84] followed by Xia et al.[85] have shown the insertion of C≡NR into unsaturated metallacycles, which lead to the formation of η^2-iminoketenyl complexes (Figure 1G). Our group also recently reported the reactivity of 1-adamantyl isonitrile (C≡NAd) with vanadium alkylidyne complexes[86,87] to form novel insertion products such as a κ^1-*N*-ynamide and a κ^2-*C*,*N*-azaalleneyl ligands (Figure 1H,I).[88] These complexes displayed different binding modes and thus exhibited different spin states using the same ligand scaffold [AdNCC^{t}Bu]$^-$. Due to our

Received: October 15, 2024
Revised: November 20, 2024
Accepted: November 25, 2024
Published: December 16, 2024



https://doi.org/10.1021/acs.organomet.4c00442
Organometallics 2025, 44, 279−288

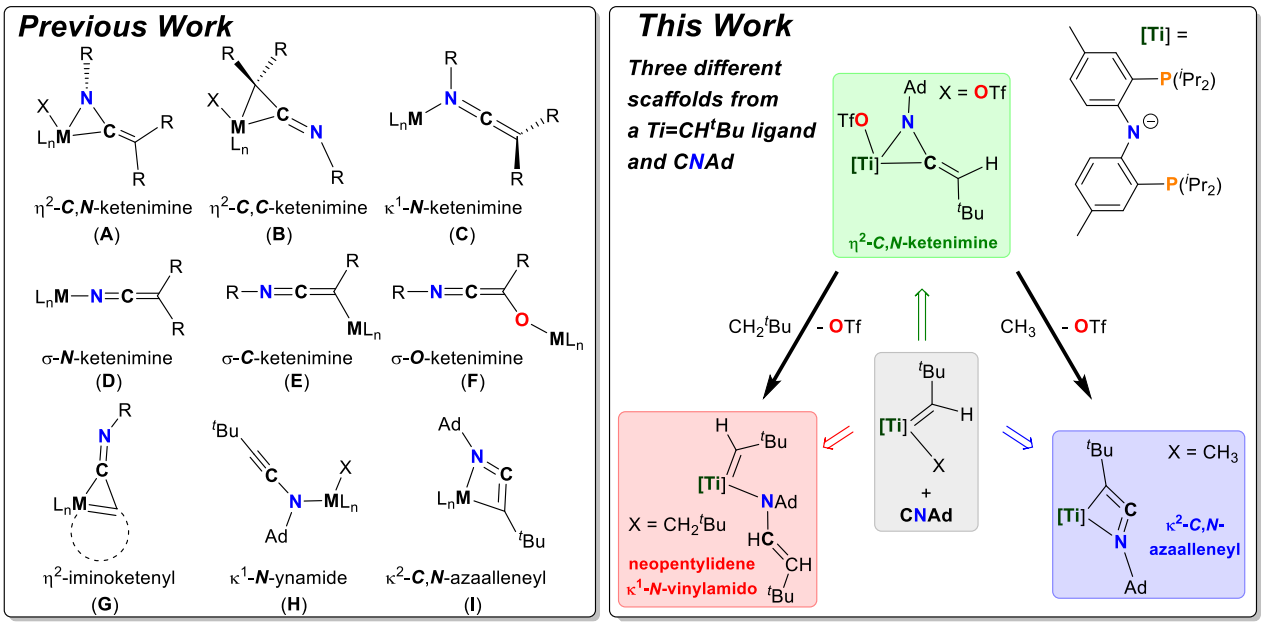


Figure 1. Left: previous work and selected examples of monodentate and chelating NCC-based ligands (ketenimine, iminoketenyl, ynamide, and azaalleneyl) synthesized via MCMB reactions with C≡NR. Right: our work describing the diverse reactivity of [(PNP)Ti=CH^{t}Bu(X)] with C≡NAd to form a η^2-*C,N*-ketenimine, neopentylidene κ^1-*N*-vinylamido, and κ^2-*C,N*-azaalleneyl scaffolds.

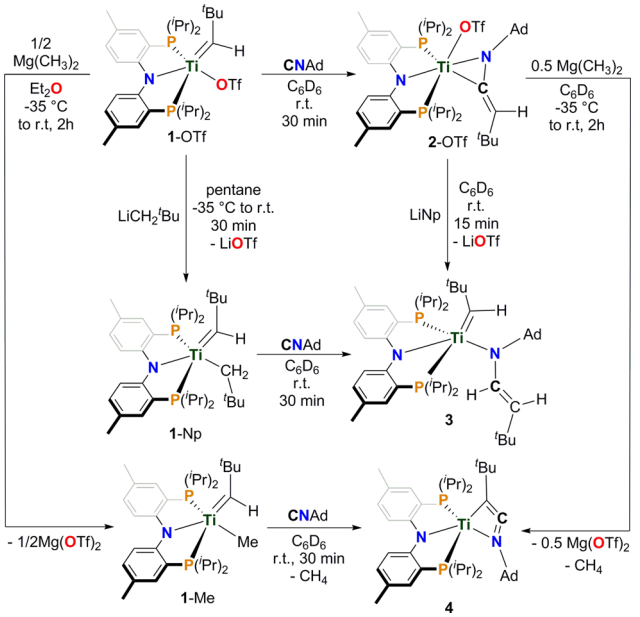
recent discoveries of new insertion complexes of C≡NR into MCMBs we decided to investigate the reactivity of C≡NR with titanium neopentylidenes, [(PNP)Ti=CH^{t}Bu(X)] (where X$^-$ = OTf (**1**-OTf), CH$_2{}^t$Bu (**1**-Np), and CH$_3$ (**1**-Me).[89−91] Likewise, previous studies with this system have shown that the PNP (PNP$^-$ = N[2-P^{i}Pr$_2$-4-methylphenyl]$_2^-$) ligand scaffold can generate a transient titanium neopentylidyne {(PNP)Ti≡C^{t}Bu}.[89,90] By utilizing the diverse reactivity of the titanium neopentylidene and neopentylidene alkyl scaffolds, our aim was to uncover novel binding modes resulting from isonitrile insertion into these MCMBs. Herein, we describe the synthesis of a η^2-*C,N*-ketenimine, a neopentylidene κ^1-*N*-vinylamido, and a rarely reported κ^2-*C,N*-azaalleneyl complexes, all of which derive from the insertion of C≡NAd into titanium neopentylidene complexes. Surprisingly, the results shown here do not suggest the involvement of a transient titanium neopentylidyne {(PNP)Ti≡C^{t}Bu}.[89,90]

RESULTS AND DISCUSSION

Synthesis of the Titanium η^2-*C,N*-Ketenimine (2-OTf). Before probing the reactivity of the C≡NAd with {(PNP)-Ti≡C^{t}Bu} or titanium neopentylidene alkyl motifs we investigated the reactivity of the titanium neopentylidene triflate complex, **1**-OTf. The reaction of **1**-OTf with one equivalent of C≡NAd in deuterated benzene (C$_6$D$_6$) at room temperature led to an immediate color change from red to violet. After workup of the reaction mixture, crystallization of the product was performed by slow concentration of a pentane solution of the reaction mixture using toluene as the sorbent at −35 °C overnight, affording needlelike violet-colored crystals of a side-on titanium η^2-*C,N*-ketenimine, (PNP)Ti(η^2-*C,N*-AdNCCH^{t}Bu)(OTf) (**2**-OTf) in a 79% yield (Scheme 1).

The ^{31}P{^{1}H} NMR spectrum of **2**-OTf displays two doublets centered at δ 28.8 and 23.2 ($^2J_{PP}$ = 77 and 79 Hz, respectively) (Figure S4), which agrees with the molecule lacking C_2 symmetry in solution. The spectroscopic resonances in the ketenimine fragment were identified by using ^{1}H−^{13}C HSQC

Scheme 1. Synthesis of Complexes 2-OTf, 3, and 4 from Neopentylidene Precursors 1-OTf, 1-Np, and 1-Me, Respectively and the Isonitrile, C≡NAd[a]



[a]Independent synthesis of complexes **3** and **4** from **2**-OTf and LiNp or 1/2 MgMe$_2$ are also shown.

(Figures 2 and S7) and ^{1}H−^{13}C HMBC (Figure S8) experiments. Highlighted in Figure 2 is the one-bond correlation of the hydrogen on the ketenimine at δ 5.16 to the β-carbon (C$_\beta$) (C$_{28}$ in Figure 3, left) at δ 110.49. The ^{1}H−^{13}C HMBC experiment confirmed this assignment of this resonance as the proton at δ 5.16 exhibits two bond correlation with the α-carbon (C$_\alpha$) (C$_{27}$ in Figure 3, left) on the η^2-*C,N*-ketenimine ligand at δ 189.70. These assignments are in good agreement with the previously characterized η^2-*C,N*-keteni-

https://doi.org/10.1021/acs.organomet.4c00442
Organometallics 2025, 44, 279−288

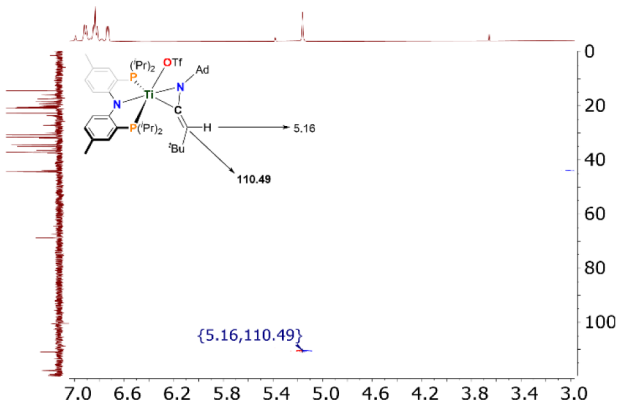


Figure 2. Partial $^{1}H-^{13}C$ HSQC NMR ((500 MHz, 126 MHz), C_6D_6, 300 K) of complex **2**-OTf, highlighting the one bond correlation in the η^2-***C,N***-ketenimine fragment.

mine complex, (BDI)Ti(η^2-***C,N***-^{t}Bu**NC**CH^{t}Bu)(OTf)[71] (where BDI$^-$ = [ArNC(CH$_3$)]$_2$CH$^-$, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$), which exhibited a ^{1}H resonance at δ 5.82 and ^{13}C resonances at δ 100.4 (for C_α) and δ 170.0 (for C_β). The η^2-***C,N***-coordination of the η^2-***C,N***-ketenimine in **2**-OTf was further confirmed by single-crystal X-ray diffraction studies (scXRD, Figure 3, left). The $C_{27}-C_{28}$ (1.353(3) Å) and $C_{27}-N_2$ (1.375(2) Å) bond distances in **2**-OTf are similar to those of other structurally characterized η^2-***C,N***-ketenimine complexes (1.35−1.37 Å and 1.33−1.37 Å, respectively).[71,86,92,93] Infrared spectroscopic studies also reveal a ν(CN) vibration for the η^2-***C,N***-ketenimine at 1463 cm^{-1} (Figure S25). This stretch compares well to the η^2-***C,N***-ketenimine complex [(P$_2$Cp)Zr-(η^2-***C,N***-^{t}Bu**NC**CHPh)(Cl)][70] which exhibits a ν(CN) at 1504 cm^{-1}, where P$_2$Cp$^-$ = η^5-C$_5$H$_3$-1,3-(SiMe$_2$CH$_2$P^{i}Pr$_2$)$_2^-$.

Synthesis of the Titanium Neopentylidene κ^1-*N*-Vinylamido (3). We then turned our attention to the neopentylidene alkyl complexes [(PNP)Ti=CH^{t}Bu(R)][89,90] (R = CH$_2^t$Bu, **1**-Np; R = CH$_3$, **1**-Me), since these species are known to undergo α-hydrogen abstraction to form the reactive and transient titanium neopentylidyne {(PNP)Ti≡C^{t}Bu}.[89] It should be noted however, that complex **1**-Np undergoes a first-order extrusion of neopentane (NpH) with a $t_{1/2}$ of ∼3.1 h at r.t.[89] whereas **1**-Me extrudes methane (CH$_4$) very slowly with a $t_{1/2}$ of ∼62.4 h at 60 °C.[90] We anticipated that such a large discrepancy in the rate of formation of the {(PNP)Ti≡C^{t}Bu}motif should allow for distinct reactivity of **1**-Np versus **1**-Me with C≡NR, since the former is more likely to produce the neopentylidyne than the latter. As a result, C≡NR could react with the Ti≡C linkage in the latter as opposed to the Ti=C or Ti−R bonds in the case of a slower α-hydrogen abstraction step. As shown in Scheme 1, complex **1**-Np[90] is readily prepared according to published procedures by triflate ligand substitution with LiNp, whereas **1**-Me[91] is prepared with half an equivalent of MgMe$_2$. Accordingly, treatment of **1**-Np with one equivalent of C≡NAd in C_6D_6 resulted in an immediate reaction at room temperature, which was accompanied by a color change from green-brown to yellow. The workup of the reaction mixture afforded a titanium neopentylidene complex containing a κ^1-***N***-vinylamido ligand, namely (PNP)Ti=CH^{t}Bu(κ^1-***N***-Ad**N**CHCH^{t}Bu) (**3**) (Scheme 1, middle), in an 84% isolated yield. Surprisingly, the reaction does not result in loss of NpH, implying that C≡NAd rapidly reacts with the titanium neopentylidene before an α-hydrogen abstraction ensues. Crystallization of **3** was performed by slow concentration of a pentane solution of the reaction mixture using toluene as the sorbent at −35 °C overnight, affording block shaped orange crystals. The ^{1}H (Figure S9), ^{1}H−^{1}H COSY (Figure S14), ^{1}H−^{13}C HSQC (Figure 4), and ^{1}H−^{13}C HMBC (Figure S17) NMR spectra of

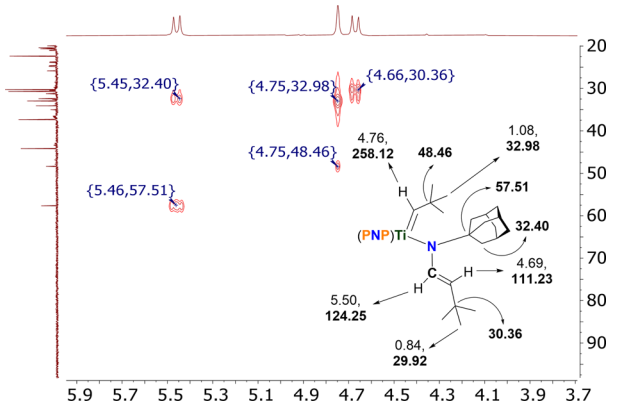


Figure 4. A partial $^1H-^{13}C$ HSQC NMR ((500 MHz, 126 MHz), C_6D_6, 300 K) of **3** (from the addition of C≡NAd to **1**-Np), highlighting the correlation of the hydrogens on the neopentylidene and the κ^1-***N***-vinylamido fragments.

3 displayed three salient spectral signals consistent with the formation of a neopentylidene κ^1-***N***-vinylamido complex. The neopentylidene resonances (^{1}H, ^{13}C) arise at δ 4.75 and 258.13, respectively, and are similar to those of other [Ti^{IV}] neopentylidene complexes reported by our group using the PNP ligand (δ 260−276).[89,94−96] The κ^1-***N***-vinylamido

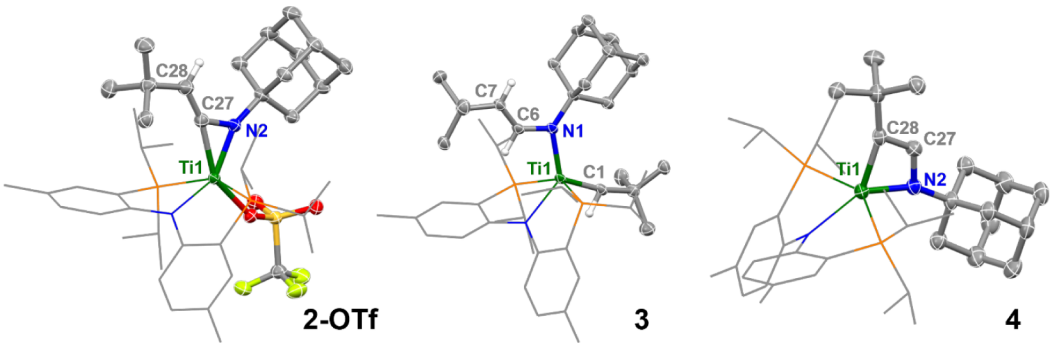


Figure 3. scXRD of **2**-OTf, **3**, and **4** with thermal ellipsoids shown at the 50% probability level (except for the PNP fragment which is shown in a wireframe). Only hydrogen atoms derived from the neopentylidene, κ^1-***N***-vinylamido, and η^2-***C,N***-ketenimine groups are shown for clarity.

https://doi.org/10.1021/acs.organomet.4c00442
Organometallics 2025, 44, 279−288

exhibits two resonances that exist as doublets ($^3J_{HH}$ = 14 Hz) at δ 5.46 and 4.67, which is in accord with previously isolated κ^1-*N*-vinylamido complexes having *trans* isomerism ($^3J_{HH}$ = 14−18 Hz).[97,98] The ^{1}H−^{13}C HSQC spectrum (Figure 4) shows that the κ^1-*N*-vinylamido protons exhibit one bond coupling to carbon resonances at δ 124.31 and 111.04, respectively. While the ^{1}H−^{13}C HMBC allowed us to distinguish between the C_β and C_γ on the κ^1-*N*-vinylamido (C_6 and C_7 in Figure 3, middle). The resonance at δ 4.67 exhibits a two-bond coupling to the resonance assigned as the central carbon of the ^{t}Bu fragment in the κ^1-*N*-vinylamido. While the resonance at δ 5.46 exhibits three-bond coupling to the apical carbon on the Ad fragment in the κ^1-*N*-vinylamido. Thus, with this information, we have tentatively assigned the resonances for the proton on C_β at δ 5.45 and the proton on the C_γ at δ 4.67. Further confirmation of complex **3** having neopentylidene and κ^1-*N*-vinylamido fragments was confirmed by scXRD (Figure 3, middle). As expected, the titanium neopentylidene Ti_1−C_1 bond distance was short, at 1.886(3) Å and comparable to previously characterized titanium neopentylidenes supported by the PNP$^-$ ligand scaffold (1.790−1.883 Å).[89,91,99] The crystallographic features of the κ^1-*N*-vinylamido fragment in **3** (Ti_1−N_1: 1.982(2) Å and C_6−C_7: 1.337(3) Å) are in good agreement with previously characterized niobium- (Nb−N: 2.037−2.097 Å, C═C: 1.336−1.349 Å)[97,100] and hafnium- (Hf−N: 2.182 Å and C═C: 1.329 Å)[101] κ^1-*N*-vinylamido complexes.

Synthesis of the Titanium κ^2-*C,N*-Azaalleneyl Complex (4). The neopentylidene alkyl complexes **1**-Np and **1**-Me have been investigated extensively in the context of C−H activation.[71,89,91,96,102−108] Specifically, complex **1**-Np failed to produce {(PNP)Ti≡C^{t}Bu} in the presence of a C≡NAd, which reacted instead at the neopentylidene linkage to form **3** (*vide infra*). This was rather surprising since the isomeric and bulky nitriles (N≡CR; R = ^{t}Bu, Ad) have been shown to undergo [2 + 2] cycloaddition chemistry across the {(PNP)-Ti≡C^{t}Bu} to generate the κ^2-*C,N*-azametallacyclobutadiene complexes of the type (PNP)Ti(κ^2-*C,N*-^{t}Bu**C**C(R)**N**) (R = ^{t}Bu, Ad).[95] To probe how reactivity would change with C≡NAd, we examined the more kinetically stable alkylidyne precursor **1**-Me. Accordingly, the reaction of **1**-Me with one equivalent of C≡NAd in C_6D_6 at room temperature led to an immediate color change from yellow to red. After workup of the reaction mixture, crystallization of the product was performed by slow concentration of a pentane solution of the reaction mixture using toluene as the sorbent at −35 °C overnight, and afforded red colored and block-like crystals of the titanium κ^2-*C,N*-azaalleneyl (PNP)Ti(κ^2-*C,N*-Ad**N**C**C**^{t}Bu) (**4**) (Scheme 1, bottom) in 95% isolated yield. Notably, the ^{13}C NMR spectrum (Figure S20) provided an interesting insight into the κ^2-*C,N*-azaalleneyl scaffold revealing the β-carbon (C_{27} of Figure 3, right) to resonate at δ 193.76, and the α-carbon (C_{28} of Figure 3, right) to resonate even further downfield at δ 228.82, which we have tentatively assigned. The α-carbon resonance is quite broad; thus, we were fortunate to confirm its assignment with the aid of an ^{1}H−^{13}C HMBC experiment (Figure 5). Interestingly, the spectroscopic data showed that there was a three-bond correlation between the protons on the ^{t}Bu fragment at δ 1.69 and the α-carbon at δ 228.82. These resonances differ quite substantially to the previously isolated vanadium κ^2-*C,N*-azaalleneyl complex (dBDI)V(κ^2-*C,N*-Ad**N**C**C**^{t}Bu) (where dBDI^{2-} = ArNC(CH$_3$)-CHC(CH$_2$)NAr, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).[88] We speculate that the difference in the chemical shifts for the α-carbon and β-carbon on the κ^2-*C,N*-azaalleneyl could be attributed to the supporting ligand scaffold (PNP$^-$ vs dBDI^{2-}) and the geometry around the metal center (trigonal bipyramidal vs tetrahedral). This trend in the difference in chemical shifts in metallacyclic complexes has been discussed by Reiß, Beweries et al.[109] in the context of all carbon based κ^2-*C,C*-deprotiometallacyclobutadienes (dMCBD). Further evidence for chelation of the κ^2-*C,N*-azaalleneyl in **4** was confirmed by scXRD (Figure 3, right). The C_{27}−C_{28} and C_{27}−N_2 bond lengths for **4** are 1.407(3) Å and 1.383(3) Å, respectively, and are longer when compared to the vanadium κ^2-*C,N*-azaalleneyl complex (C−C and C−N bond lengths of 1.394(2) Å and 1.331(2) Å, respectively). The Ti_1−C_{28} bond length of **4** (1.926(2)Å) is longer than the vanadium κ^2-*C,N*-azaalleneyl bond length of 1.843(2) Å, while the M−N bond lengths are quite similar (1.872(2) Å, M = Ti (**4**) and 1.877(1) Å, M = V[88]). Lastly, the κ^2-*C,N*-azaalleneyl in **4** displays a bond angle of 121.9(2)° ($\angle N_2$−C_{27}−C_{28}) and is more acute than the vanadium κ^2-*C,N*-azaalleneyl bond angle of 127.6(2)°, which we attribute to the increased steric demand of the PNP ligand scaffold in comparison to the dBDI^{2-} ligand scaffold as well as the greater coordination number in complex **4**.

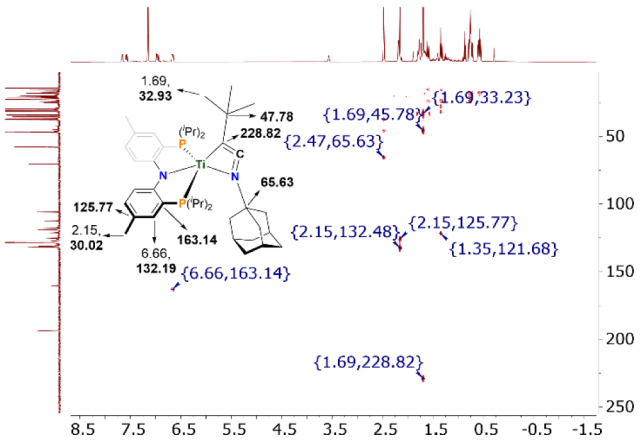


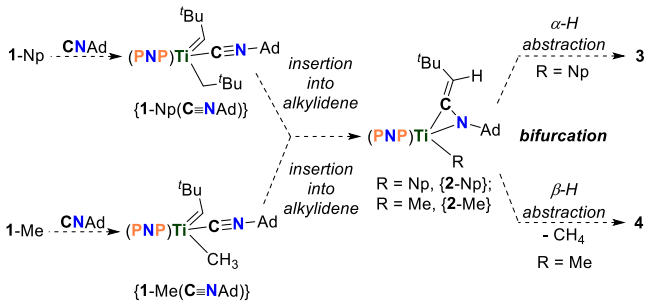
Figure 5. ^{1}H−^{13}C HMBC ((500 MHz, 126 MHz), C_6D_6, 300 K) for complex **4** (from the addition of C≡NAd to **1**-Me), which highlights the two and three bond correlation of the hydrogens on the ^{t}Bu fragment to carbon atoms on the complex.

A Bifurcated Reaction Pathway Involving the η^2-*C,N*-Ketenimine Moiety. Despite being alkylidyne synthons, complexes **1**-Np and **1**-Me react quite differently with C≡NAd to yield insertion products **3** and **4**. However, we have noted in a previous study involving the reactivity of N≡CR and **1**-Np, that subtle changes in the steric environment can drastically alter the outcome in the products.[95] For instance, complex **1**-Np extrudes NpH to form {(PNP)Ti≡C^{t}Bu} in the presence of sterically demanding N≡CR, whereas the use of less sterically hindered N≡CR (R = Ph, ^{i}Pr) generate instead titanium imide alkyls, (PNP)Ti═NC(R)CH^{t}Bu-(CH$_2$^{t}Bu) (R = Ph, ^{i}Pr) from cycloaddition chemistry involving the titanium neopentylidene ligand. In our present study, we propose a bifurcated pathway to complexes **3** and **4**, respectively. Both mechanisms are speculated to proceed through three key elementary steps. Regardless of the alkyl group on the titanium neopentylidene, the first two proposed steps involve C≡NAd coordination to the metal center to form transient {**1**-R(C≡NAd)} (R = Me, Np) followed by

https://doi.org/10.1021/acs.organomet.4c00442
Organometallics 2025, 44, 279−288

rapid insertion of the C≡NAd into the titanium neopentylidene ligand to generate an η^2-*C*,*N*-ketenimine fragment as outlined in Scheme 2. We speculate the first two steps to

Scheme 2. Proposed Mechanism for the Formation of Complexes 3 (Top) and 4 (Bottom) with Intermediates Drawn[a]



[a]Replacing the R group from CH_3 (Me) with $CH_2{}^tBu$ (Np) results in a bifurcated process where α-hydrogen abstraction switches to β-hydrogen abstraction.

proceed in a similar fashion for both **3** and **4**, resulting in intermediate {(PNP)Ti(η^2-*C*,*N*-Ad**N**C**C**H^{t}Bu)(R)} (**2**-R; R = Np, {**2**-Np} and R = Me, {**2**-Me}) as outlined in Scheme 2. It is at this step, where the system should result in a bifurcated process. If {**2**-R} is a common intermediate in these reactions, a transmetalation with the appropriate alkylating reagent should allow us to traverse from **2**-OTf to the intermediate species {**2**-R}, and ultimately to **3** and **4**. To probe this proposed mechanism, we explored the reaction of **2**-OTf with one equivalent of LiNp in C_6D_6. Accordingly, upon addition of a solution of **2**-OTf to LiNp a color change occurred immediately from violet to yellow. A ^{1}H and a ^{31}P{^{1}H} NMR spectrum was taken shortly thereafter which indicated quantitative conversion to **3**. A similar procedure was applied to access complex **4** cleanly, by the addition of one-half equivalent of dimethyl magnesium ($MgMe_2$) to **2**-OTf, resulting in an immediate color change from violet to red with the coevolution of methane gas (CH_4) and the precipitation of a solid we speculate to be lithium triflate, LiOTf.

In the case of **1**-Me and C≡NAd, where CH_4 is liberated, we argue against α-hydrogen abstraction preceding C≡NAd insertion into the alkylidyne ligand of transient {(PNP)Ti≡C^{t}Bu}, since the rate of this reaction is too fast (seconds) compared to previous mechanistic studies involving the formation of from either **1**-Np (hours)[89] and **1**-Me (days).[90] Our independent studies argue for {**2**-R} involving a bifurcated process, and changing course depending on the R fragment to ultimately form **3** and **4**. In the case of **3**, an α-hydrogen abstraction occurs to form the corresponding neopentylidene κ^1-*N*-vinylamido, **3** (top of Scheme 2). Akin to **3**, one could propose that an intermediate {**1**-Me(C≡NAd)} would undergo a similar transformation to a methylidene κ^1-*N*-vinylamido complex {(PNP)Ti=CH$_2$(κ^1-*N*-Ad**N**CHC^{t}Bu)}. However, one must first take into account the energetic differences of accessing a methylidene versus a neopentylidene through an α-hydrogen abstraction.[11,110,111] Due to the unfavorable energetics in accessing a methylidene on the titanium metal center, we suggest that the system instead traverses through a β-hydrogen abstraction to deliver complex **4**. Such a β-hydrogen abstraction results in the loss of methane in accordance with our experimental observations (bottom of Scheme 2). Previous studies by Schrock,[2,11,112,113] and us[114] have demonstrated that the α-hydrogen abstraction pathway is generally favored when β-hydrogens in the adjacent ligand are lacking. In these studies, our proposed η^2-*C*,*N*-ketenimine intermediates {**2**-Np} and {**2**-Me} possess β-hydrogens on the side-on ketenimine, but the alkane is only eliminated when the alkyl group is a CH_3. This argues against thermodynamics involving the Ti−Np versus the more stable Ti−Me bond as detailed by Wolczanski.[115] In other words, the system chooses to pay a lower enthalpic penalty in order to avoid making the more reactive titanium methylidene ligand.

CONCLUSION

In this report we discussed the reactivity of a bulky isonitrile, C≡NAd with titanium neopentylidene complexes. Contrasting earlier results involving the reaction of **1**-Np with N≡CR, we establish here the formation of η^2-*C*,*N*-, κ^1-*N*-, and κ^2-*C*,*N*-organometallic scaffolds with C≡NAd. We also propose common intermediates to be formed from the binding of C≡NAd to the titanium metal center, and subsequent insertion into the titanium neopentylidene fragment to form a η^2-*C*,*N*-ketenimine fragment. However, the resulting reactivity of this η^2-*C*,**N**-ketenimine fragment varies depending on the alkyl group bound to the titanium metal center. Intuitively, when a triflate ligand is present no further reactivity occurs (**2**-OTf), whereas the presence of a Np ligand yields α-hydrogen abstraction generating a neopentylidene κ^1-*N*-vinylamido complex. In the case of a Me ligand, we gain access to a rarely reported κ^2-*C*,*N*-azaalleneyl complex, via a β-hydrogen abstraction pathway, to avoid the higher energy pathway that results in formation of a reactive titanium methylidene ligand.

EXPERIMENTAL SECTION

All operations were performed in a Labmaster 130 glovebox or using standard Schlenk techniques under a nitrogen atmosphere unless otherwise stated. Pentane and toluene (Fisher Scientific) were purchased from commercial vendors, thoroughly bubbled with argon, and made anhydrous by passage through columns of activated alumina in a Grubbs-type solvent system. All anhydrous solvents were stored over sodium metal and 4 Å molecular sieves. Benzene-d_6 (C_6D_6, Cambridge Isotope Laboratories) was dried over a potassium mirror, vacuum transferred to a flame-dried flask and degassed by freeze−pump−thaw cycles prior to use. Celite and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. **1**-OTf,[99] **1**-Np,[90] and **1**-Me[91] were prepared according to published procedures. 1-adamantyl isonitrile (C≡NAd, Ad = $C_{10}H_{15}$, Sigma-Aldrich, 95%) was used as received.

Crystallographic studies were carried out on single crystals, which were coated with paratone oil, mounted at the end of a cryoloop, and placed in the nitrogen cold stream at 100 K. Data were collected and processed using Bruker ApexII, Rigaku XtaLAB Synergy-I, or Rigaku XtaLAB Synergy-S diffractometers (Mo K_α radiation), operated through the manufacturer's software. The crystal structures were solved using SHELXT (intrinsic phasing) and refined using SHELXL-2018 (least-squares) typically with data processing carried out in Olex2

NMR spectroscopic studies were recorded on Bruker NEO 600 MHz, AVIII Bio500, UNI400 or AVIII 500 MHz spectrometers. ^{1}H and ^{13}C NMR chemical shifts are referenced to the internal proton or carbon resonances of C_6D_6 (δ 7.16 and 128.06). ^{31}P NMR chemical shifts are reported with respect to external H_3PO_4 (aqueous solution, δ 0.0). ^{19}F NMR chemical shifts are referenced using ^{1}H spectrum as an absolute reference utilizing the IUPAC unified scale which relies on Ξ values expressed as percentages.

https://doi.org/10.1021/acs.organomet.4c00442
Organometallics 2025, 44, 279−288

FT−IR spectroscopic studies were measured on a JASCO FT/IR-4600 spectrometer with samples mounted between KBr windows using the JASCO tablet master device. The sample chamber was flushed with argon gas to prevent decomposition during measurements.

Synthesis of (PNP)Ti(η^2-*C,N*-AdNCCH^{t}Bu)(OTf) (2-OTf). (PNP)Ti=CH^{t}Bu(OTf) (**1**-OTf) (50.4 mg, 72.5 μmol, 1.00 equiv) was dissolved in ca. 0.5 mL of C_6D_6 and the solution was added to a vial containing C≡NAd (11.7 mg, 72.5 μmol, 1.00 equiv) in ca. 0.5 mL of C_6D_6 under vigorous stirring. The color of the solution changed from a red to a dark violet instantaneously. The content of the vial was stirred for 30 min and was subsequently cooled to −35 °C. The C_6D_6 was lypholized under dynamic vacuum and the residue was extracted into ca. 5 mL of pentane and was filtered over Celite and the Celite was washed with ca. 5 mL pentane. The pentane solution was then concentrated to ca. 1 mL. The concentrated solution was transferred into a small crystallization vial and placed in a large vial containing toluene. The combined vials were cooled to −35 °C overnight resulting in the formation of violet crystals identified as (PNP)Ti(η^2-*C,N*-Ad**NC**CH^{t}Bu)(OTf) (**2**-OTf). Crystals suitable for X-ray crystallography were separated from a pentane solution of **2**-OTf. Yield: 49.0 mg, 57.2 μmol, 79.0% based on **1**-OTf. ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ 7.32−7.48 (m, 2H, C_6H_3), 6.73−6.93 (m, 4H, C_6H_3), 5.17 (s, 1H, (η^2-*C,N*-AdNCC*H*^{t}Bu), 2.76−2.85 (m, 6H, Ad), 2.65−2.73 (sept, 2H, C*H*(CH$_3$)$_2$), 2.36−2.44 (sept, 2H, C*H*(CH$_3$)$_2$), 2.23−2.33 (m, 3H, Ad), 2.17 (s, 3H, C_6H_3−C*H*$_3$), 2.08 (s, 3H, C_6H_3−C*H*$_3$), 1.81−1.90 (m, 3H, Ad), 1.66−1.73 (m, 3H, Ad), 1.10−1.42 (m, 20H, CH(C*H*$_3$)$_2$), 0.99−1.04 (m, 4H, CH-(C*H*$_3$)$_2$), 0.86 (s, 9H, C(C*H*$_3$)$_3$), 0.75−0.83 (m, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (126 MHz, C_6D_6, 300 K): δ 189.99 (broad s, η^2-*C,N*-AdNCCH^{t}Bu), 161.68 (s, C_6H_3), 159.53 (s, C_6H_3), 133.56 (s, C_6H_3), 133.19 (s, C_6H_3), 132.06 (s, C_6H_3), 131.25 (s, C_6H_3), 121.55 (d, C_6H_3), 119.71 (s, C_6H_3), 119.49 (d, C_6H_3), 117.81 (d, C_6H_3), 110.95 (s, η^2-*C,N*-AdNCCH^{t}Bu), 68.75 (s, η^2-*C,N-Ad*NCCH^{t}Bu), 44.29 (s, η^2-*C,N-Ad*NCCH^{t}Bu), 43.95 (s, η^2-*C,N-Ad*NCCH^{t}Bu), 37.39 (s, η^2-*C,N-Ad*NCCH^{t}Bu), 37.19 (s, η^2-*C,N-Ad*NCCH^{t}Bu), 36.47 (s, η^2-*C,N-Ad*NCCH^{t}Bu), 34.96 (s, η^2-*C,N-Ad*NCCH^{t}Bu), 34.44 (s, η^2-*C,N-Ad*NCCH^{t}Bu), 31.92 (d, CH(CH$_3$)$_2$), 31.64 (s, η^2-*C,N*-AdNCCH^t*Bu*), 30.84 (s, η^2-*C,N*-AdNCCH^t*Bu*), 30.75 (s, CH-(*C*H$_3$)$_2$), 30.15 (s, η^2-*C,N-Ad*NCCH^{t}Bu), 27.15 (d, *C*H(CH$_3$)$_2$), 23.63 (d, *C*H(CH$_3$)$_2$), 20.91 (s, CH(CH$_3$)$_2$), 20.78 (s, CH(*C*H$_3$)$_2$), 20.70 (d, C_6H_3−*C*H$_3$), 20.57 (s, CH(*C*H$_3$)$_2$), 20.06 (d, C_6H_3−*C*H$_3$), 19.16 (d, CH(*C*H$_3$)$_2$), 18.46 (d, CH(*C*H$_3$)$_2$), 17.43 (d, CH(*C*H$_3$)$_2$), 15.96 (d, CH(*C*H$_3$)$_2$). ^{31}P NMR (131 MHz, C_6D_6, 300 K): δ 28.8 (dd, PNP, J_{P-P} = 77 Hz), 23.3 (dd, PNP, J_{P-P} = 79 Hz). ^{19}F NMR (282 MHz, C_6D_6, 300 K): δ −75.1 (s, OSO_2CF_3). IR, solid, ν (cm^{-1}): 1463 (C−N stretch).

Synthesis of (PNP)Ti=CH^{t}Bu(κ^1-*N*-AdNCHCH^{t}Bu) (3). *Pathway A.* (PNP)Ti=CH^{t}Bu(Np) (**1**-Np) (25.3 mg, 41.0 μmol, 1.00 equiv) was dissolved in ca. 0.5 mL of C_6D_6 and the solution was added to a vial containing C≡NAd (6.60 mg, 41.0 μmol, 1.00 equiv) in ca. 0.5 mL of C_6D_6 under vigorous stirring. The solution changed from brown-green to yellow instantaneously. The content of the vial was stirred for 30 min and was subsequently cooled to −35 °C. The C_6D_6 was lypholized under dynamic vacuum and the residue was extracted into ca. 5 mL of pentane and was filtered over Celite and the Celite was washed with ca. 5 mL pentane. The pentane solution was then concentrated to ca. 1 mL. The concentrated solution was transferred into a small crystallization vial and placed in a large vial containing toluene. The combined vials were cooled to −35 °C overnight resulting in the formation of orange crystals identified as (PNP)Ti=CH^{t}Bu(κ^1-*N*-Ad**N**CHCH^{t}Bu) (**3**). Crystals suitable for X-ray crystallography were separated from a pentane solution of **3**. Yield: 26.6 mg, 34.2 μmol, 83.5% based on (**1**-Np). ^{1}H NMR (500 MHz, C_6D_6, 300 K): 7.23−7.28 (m, 2H, C_6H_3), 6.91−6.93 (m, 2H, C_6H_3), 6.81−6.83 (m, 2H, C_6H_3), 5.46 (d, 1H, κ^1-*N*-AdNC*H*CH^{t}Bu), 4.76 (s, 1H, Ti=C*H*^{t}Bu), 4.67 (d, 1H, κ^1-*N*-AdNCHCH^{t}Bu), 2.53−2.63 (m, 6H, Ad), 2.51 (sept, 2H, C*H*(CH$_3$)$_2$), 2.35 (sept, 2H, C*H*(CH$_3$)$_2$), 2.28 (m, 3H, Ad), 2.22 (s, 3H, C_6H_3−C*H*$_3$), 2.18 (s, 3H, C_6H_3−C*H*$_3$), 1.74−1.87 (m, 6H, Ad), 1.61−1.66 (m, 8H, CH(C*H*$_3$)$_2$), 1.33−1.46 (m, 16H, CH(C*H*$_3$)$_2$), 1.10 (s, 9H, C(C*H*$_3$)$_3$), 0.86 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR (126 MHz, C_6D_6, 300 K): 258.48 (t, Ti=*C*H^{t}Bu), 161.39 (d, C_6H_3), 157.97 (d, C_6H_3), 132.38 (s, C_6H_3), 132.15 (s, C_6H_3), 130.82 (s, C_6H_3), 126.68 (t, C_6H_3), 124.62 (s, κ^1-*N*-AdN*C*HCH^{t}Bu), 124.01 (d, C_6H_3), 122.34 (d, C_6H_3), 119.12 (d, C_6H_3), 116.91 (d, C_6H_3), 111.33 (s, κ^1-*N*-AdNCH*C*H^{t}Bu), 58.03 (s, κ^1-*N-Ad*NCHCH^{t}Bu), 48.71 (s, κ^1-*N-Ad*NCHCH^{t}Bu), 44.54 (s, κ^1-*N-Ad*NCHCH^{t}Bu), 37.69 (s, κ^1-*N-Ad*NCHCH^{t}Bu), 35.38 (s, κ^1-*N-Ad*NCHCH^{t}Bu), 32.78 (s, Ti=CH(*C*H$_3$)$_3$), 31.61 (s, κ^1-*N-Ad*NCHCH^{t}Bu), 31.05 (s, κ^1-*N-Ad*NCHCH^{t}Bu), 30.60 (s, κ^1-*N*-AdNCHCH^t*Bu*), 26.22 (d, CH-(*C*H$_3$)$_2$), 25.11 (d, CH(*C*H$_3$)$_2$), 24.93 (d, CH(*C*H$_3$)$_2$), 21.38 (d, CH(*C*H$_3$)$_2$), 21.02 (C_6H_3−*C*H$_3$), 20.77 (C_6H_3−*C*H$_3$), 20.31 (d, CH(*C*H$_3$)$_2$), 20.19 (s, C_6H_3−*C*H$_3$), 19.94 (d, CH(*C*H$_3$)$_2$), 19.77 (d, CH(*C*H$_3$)$_2$), 19.26 (d, CH(*C*H$_3$)$_2$), 18.78 (d, CH(*C*H$_3$)$_2$), 16.03 (d, CH(*C*H$_3$)$_2$). ^{31}P NMR (131 MHz, C_6D_6, 300 K): 31.5 (dd, J_{P-P} = 53 Hz), 24.2 (dd, J_{P-P} = 53 Hz). IR, solid, ν (cm^{-1}): 1506 (C=C stretch), 1460 (C−N stretch), 1278 (C−N stretch).

Pathway B. In a J-Young NMR tube (PNP)Ti(η^2-*C,N*-Ad**NC**CH^{t}Bu)(OTf) (**2**-OTf) (17.1 mg, 16.8 μmol, 1.00 equiv) was added and was dissolved in ca. 0.5 mL of C_6D_6. The solution was then added a C_6D_6 solution ca. 0.5 mL containing neopentyl lithium (2.0 mg, 25.6 μmol, 1.03 equiv) and the solution color changed from violet to yellow instantaneously. The NMR tube was then subjugated to NMR experiments revealing the formation of (PNP)Ti=CH^{t}Bu(κ^1-*N*-Ad**N**CHCH^{t}Bu) (**3**) quantitatively.

Synthesis of (PNP)Ti(κ^2-*C,N*-AdNCC^{t}Bu) (4). *Pathway A.* (PNP)Ti=CH^{t}Bu(Me) (**1**-Me) (30.4 mg, 51.4 μmol, 1.00 equiv) was dissolved in ca. 0.5 mL of C_6D_6 and the solution was added to a vial containing C≡NAd (8.73 mg, 54.1 μmol, l.00 equiv) in ca. 0.5 mL of C_6D_6 under vigorous stirring. The color of the solution changed from a yellow to a dark red instantaneously. The content of the vial was stirred for 30 min and was subsequently cooled to −35 °C. The C_6D_6 was lypholized under dynamic vacuum and the residue was extracted into ca. 5 mL of pentane and was filtered over Celite and the Celite washed with ca. 5 mL pentane. The pentane solution was then concentrated to ca. 1 mL. The concentrated solution was transferred into a small crystallization vial and placed in a large vial containing toluene. The combined vials were cooled to −35 °C overnight resulting in the formation of red crystals identified as (PNP)Ti(κ^2-*C,N*-Ad**NC**C^{t}Bu) (**4**) Crystals suitable for X-ray crystallography were separated from a pentane solution of **4**. Yield: 36.2 mg, 51.2 μmol, 94.6% based on **1**-Me. ^{1}H NMR (500 MHz, C_6D_6, 300 K): δ 7.57−7.69 (m, 2H, C_6H_3), 6.94−7.00 (m, 2H, C_6H_3), 6.65−6.69 (m, 2H, C_6H_3), 2.42−2.52 (m, 6H, κ^2-*C,N-Ad*NCC^{t}Bu), 2.17−2.22 (m, 3H, κ^2-*C,N-Ad*NCC^{t}Bu), 2.16 (overlapping s, 6H, C_6H_3−C*H*$_3$), 1.72−1.82 (m, 6H, κ^2-*C,N-Ad*NCC^{t}Bu), 1.70 (s, 9H, κ^2-*C,N*-AdNCC^t*Bu*), 1.58−1.63 (m, 4H, C*H*(CH$_3$)$_2$), 1.27−1.46 (m, 6H, CH(C*H*$_3$)$_2$), 0.72−0.81 (m, 12H, CH(C*H*$_3$)$_2$), 0.55−0.63 (m, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (126 MHz, C_6D_6, 300 K): 228.82 (broad s, κ^2-*C,N*-AdNCC^{t}Bu), 193.67 (broad s, κ^2-*C,N*-AdNCC^{t}Bu), 160.44 (dd, C_6H_3), 131.95 (d, C_6H_3), 131.82 (C_6H_3), 131.14 (C_6H_3), 128.60 (C_6H_3), 128.36 (C_6H_3), 128.17 (C_6H_3), 127.97 (C_6H_3), 125.36 (dd, C_6H_3), 121.36 (d, C_6H_3), 119.23 (d, C_6H_3), 119.02 (C_6H_3), 118.04 (d, C_6H_3), 70.62 (s, κ^2-*C,N*-AdNCC^t*Bu*), 57.87 (s, κ^2-*C,N*-AdNCC^t*Bu*), 47.01 (d, κ^2-*C,N-Ad*NCC^{t}Bu), 37.51 (d, κ^2-*C,N-Ad*NCC^{t}Bu), 37.18 (d, κ^2-*C,N-Ad*NCC^{t}Bu), 35.41 (d, κ^2-*C,N-Ad*NCC^{t}Bu), 34.05 (d, κ^2-*C,N-Ad*NCC^{t}Bu), 31.37 (d, κ^2-*C,N-Ad*NCC^{t}Bu), 30.72 (d, κ^2-*C,N-Ad*NCC^{t}Bu), 29.71 (d, κ^2-*C,N-Ad*NCC^{t}Bu), 25.18 (d, CH(CH$_3$)$_2$), 24.27 (CH(CH$_3$)$_2$), 22.45 (d, CH(CH$_3$)$_2$), 21.70 (d, CH(CH$_3$)$_2$), 21.35 (d, CH(CH$_3$)$_2$), 21.07 (C_6H_3−CH$_3$), 20.95 (C_6H_3−CH$_3$), 20.41 (d, CH(CH$_3$)$_2$), 19.99 (t, CH(CH$_3$)$_2$), 19.82 (d, CH(CH$_3$)$_2$), 18.16 (d, CH(CH$_3$)$_2$), 17.28 (d, CH(CH$_3$)$_2$), 15.77 (d, CH(CH$_3$)$_2$). ^{31}P NMR (131 MHz, C_6D_6,300 K): δ 16.8 (dd, J_{P-P} = 40 Hz), 15.8 (dd, J_{P-P} = 40 Hz). IR, solid, ν (cm^{-1}): 1505 (C=C stretch), 1460 (C−N stretch), 1280 (C−N stretch).

Pathway B. In a small vial (PNP)Ti(η^2-*C,N*-Ad**NC**CH^{t}Bu)(OTf) (**2**-OTf) (17.1 mg, 16.8 μmol, 1.00 equiv) was added and was dissolved in ca. 0.5 mL of C_6D_6. The solution was then added to a vial

https://doi.org/10.1021/acs.organomet.4c00442
Organometallics 2025, 44, 279−288

containing dimethyl magnesium (0.7 mg, 13.0 μmol, 0.77 equiv) and the solution color changed from yellow to red instantaneously. The NMR tube was then subjugated to NMR experiments revealing the formation of (PNP)Ti(κ^2-*C*,*N*-AdNCC^{t}Bu) (**4**) quantitatively.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.4c00442.

Synthetic procedures, NMR, IR spectra, and scXRD data (PDF)

Accession Codes

Deposition Numbers 2379006−2379008 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

■ AUTHOR INFORMATION

Corresponding Author

Daniel J. Mindiola − *Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States;* orcid.org/0000-0001-8205-7868; Email: mindiola@sas.upenn.edu

Authors

John B. Russell − *Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States;* orcid.org/0009-0004-3580-7610

Michael R. Gau − *Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States;* orcid.org/0000-0002-4790-6980

Patrick J. Carroll − *Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States;* orcid.org/0000-0002-8142-7211

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.4c00442

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. J.B.R. conducted experimental studies and characterization of all complexes and writing of the manuscript. M.R.G. and P.J.C. aided with crystallographic studies. D.J.M. supervised and funded the project along with organizing and writing the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is dedicated to Prof. Richard Schrock on the occasion of his 80th birthday. We thank the U.S. National Science Foundation (NSF; CHE-2154620 to D.J.M). J.B.R. thanks the Vagelos Institute for Energy Science and Technology (VIEST) for a predoctoral fellowship. J.B.R would also like to acknowledge Dr. Jun Gu and Dr. Chad Lawrence for their assistance in NMR experiments and spectral assignments.

■ ABBREVIATIONS

PNP$^-$, N[2-P^{i}Pr$_2$-4-methylphenyl]$_2^-$; ^{t}Bu, tertbutyl; OTf$^-$, trifluoromethanesulfonate$^-$; Ad, adamantyl; C≡NR, isonitrile; ^{i}Pr, isopropyl; C≡NAd, 1-adamantyl isonitrile; N≡CR, nitrile; NMR, nuclear magnetic resonance; HMBC, heteronuclear multiple bond correlation; HSQC, heteronuclear single quantum coherence; scXRD, single crystal X-ray diffraction; MCMBs, metal−carbon multiple bonds; dMCBD, deprotiometallacyclobutadiene; COSY, COrrelation SpectroscopY; Ph, phenyl; Np, neopentyl; NpH, neopentane; P_2Cp^-, η^5-C_5H_3-1,3-(SiMe$_2$CH$_2$P^{i}Pr$_2$)$_2^-$; Ar, aryl; {(PNP)Ti≡C^{t}Bu}, transient titanium alkylidyne

■ REFERENCES

(1) Schwab, P.; Grubbs, R. H.; Ziller, J. W. Synthesis and Applications of RuCl$_2$(CHR′)(PR$_3$)$_2$: The Influence of the Alkylidene Moiety on Metathesis Activity. *J. Am. Chem. Soc.* **1996**, *118* (1), 100−110.

(2) Schrock, R. R. Living Ring-Opening Metathesis Polymerization Catalyzed by Well-Characterized Transition-Metal Alkylidene Complexes. *Acc. Chem. Res.* **1990**, *23* (5), 158−165.

(3) Schrock, R. R.; Hoveyda, A. H. Molybdenum and tungsten imido alkylidene complexes as efficient olefin-metathesis catalysts. *Angew. Chem., Int. Ed.* **2003**, *42* (38), 4592−4633.

(4) Hoveyda, A. H.; Zhugralin, A. R. The remarkable metal-catalysed olefin metathesis reaction. *Nature* **2007**, *450* (7167), 243−251.

(5) Schrock, R. R. Multiple metal-carbon bonds for catalytic metathesis reactions (Nobel Lecture). *Angew. Chem., Int. Ed.* **2006**, *45* (23), 3748−3759.

(6) Cui, M.; Lin, R.; Jia, G. Chemistry of Metallacyclobutadienes. *Chem.—Asian J.* **2018**, *13* (8), 895−912.

(7) Heppekausen, J.; Stade, R.; Kondoh, A.; Seidel, G.; Goddard, R.; Furstner, A. Optimized synthesis, structural investigations, ligand tuning and synthetic evaluation of silyloxy-based alkyne metathesis catalysts. *Chem.—Eur. J* **2012**, *18* (33), 10281−10299.

(8) Furstner, A. Alkyne metathesis on the rise. *Angew. Chem., Int. Ed.* **2013**, *52* (10), 2794−2819.

(9) Ehrhorn, H.; Tamm, M. Well-Defined Alkyne Metathesis Catalysts: Developments and Recent Applications. *Chem.—Eur. J.* **2019**, *25* (13), 3190−3208.

(10) Ehrhorn, H.; Bockfeld, D.; Freytag, M.; Bannenberg, T.; Kefalidis, C. E.; Maron, L.; Tamm, M. Studies on Molybdena- and Tungstenacyclobutadiene Complexes Supported by Fluoroalkoxy Ligands as Intermediates of Alkyne Metathesis. *Organometallics* **2019**, *38* (7), 1627−1639.

(11) Schrock, R. R. High oxidation state multiple metal-carbon bonds. *Chem. Rev.* **2002**, *102* (1), 145−179.

(12) Lhermet, R.; Furstner, A. Cross-metathesis of terminal alkynes. *Chem.—Eur. J.* **2014**, *20* (41), 13188−13193.

(13) Gonsales, S. A.; Kubo, T.; Flint, M. K.; Abboud, K. A.; Sumerlin, B. S.; Veige, A. S. Highly Tactic Cyclic Polynorbornene: Stereoselective Ring Expansion Metathesis Polymerization of Norbornene Catalyzed by a New Tethered Tungsten-Alkylidene Catalyst. *J. Am. Chem. Soc.* **2016**, *138* (15), 4996−4999.

(14) Nadif, S. S.; Kubo, T.; Gonsales, S. A.; VenkatRamani, S.; Ghiviriga, I.; Sumerlin, B. S.; Veige, A. S. Introducing ″Ynene″ Metathesis: Ring-Expansion Metathesis Polymerization Leads to Highly Cis and Syndiotactic Cyclic Polymers of Norbornene. *J. Am. Chem. Soc.* **2016**, *138* (20), 6408−6411.

(15) Roland, C. D.; Li, H.; Abboud, K. A.; Wagener, K. B.; Veige, A. S. Cyclic polymers from alkynes. *Nat. Chem.* **2016**, *8* (8), 791−796.

(16) Miao, Z. H.; Kubo, T.; Pal, D.; Sumerlin, B. S.; Veige, A. S. pH-Responsive Water-Soluble Cyclic Polymer. *Macromolecules* **2019**, *52* (16), 6260−6265.

(17) Niu, W. J.; Gonsales, S. A.; Kubo, T.; Bentz, K. C.; Pal, D.; Savin, D. A.; Sumerlin, B. S.; Veige, A. S. Polypropylene: Now Available without Chain Ends. *Chem* **2019**, *5* (1), 237−244.

(18) Roland, C. D.; Zhang, T.; VenkatRamani, S.; Ghiviriga, I.; Veige, A. S. A catalytically relevant intermediate in the synthesis of cyclic polymers from alkynes. *Chem. Commun.* **2019**, *55* (91), 13697−13700.

(19) Miao, Z. H.; Pal, D.; Niu, W. J.; Kubo, T.; Sumerlin, B. S.; Veige, A. S. Cyclic Poly(4-methyl-1-pentene): Efficient Catalytic Synthesis of a Transparent Cyclic Polymer. *Macromolecules* **2020**, *53* (18), 7774−7782.
(20) Pal, D.; Miao, Z. H.; Garrison, J. B.; Veige, A. S.; Sumerlin, B. S. Ultra-High-Molecular-Weight Macrocyclic Bottlebrushes via Post-Polymerization Modification of a Cyclic Polymer. *Macromolecules* **2020**, *53* (22), 9717−9724.
(21) Jakhar, V.; Pal, D.; Ghiviriga, I.; Abboud, K. A.; Lester, D. W.; Sumerlin, B. S.; Veige, A. S. Tethered Tungsten-Alkylidenes for the Synthesis of Cyclic Polynorbornene via Ring Expansion Metathesis: Unprecedented Stereoselectivity and Trapping of Key Catalytic Intermediates. *J. Am. Chem. Soc.* **2021**, *143* (2), 1235−1246.
(22) Mandal, U.; Ghiviriga, I.; Abboud, K. A.; Lester, D. W.; Veige, A. S. Double Tethered Metallacyclobutane Catalyst for Cyclic Polymer Synthesis. *J. Am. Chem. Soc.* **2021**, *143* (41), 17276−17283.
(23) Miao, Z. H.; Esper, A. M.; Nadif, S. S.; Gonsales, S. A.; Sumerlin, B. S.; Veige, A. S. Semi-conducting cyclic copolymers of acetylene and propyne. *React. Funct. Polym.* **2021**, *169*, 105088.
(24) Miao, Z.; Gonsales, S. A.; Ehm, C.; Mentink-Vigier, F.; Bowers, C. R.; Sumerlin, B. S.; Veige, A. S. Cyclic polyacetylene. *Nat. Chem.* **2021**, *13* (8), 792−799.
(25) Miao, Z. H.; Konar, D.; Sumerlin, B. S.; Veige, A. S. Soluble Polymer Precursors via Ring-Expansion Metathesis Polymerization for the Synthesis of Cyclic Polyacetylene. *Macromolecules* **2021**, *54* (17), 7840−7848.
(26) Beauchamp, A. M.; Chakraborty, J.; Ghiviriga, I.; Abboud, K. A.; Lester, D. W.; Veige, A. S. Ring Expansion Alkyne Metathesis Polymerization. *J. Am. Chem. Soc.* **2023**, *145* (41), 22796−22802.
(27) Boeck, P. T.; Yadav, R.; Sumerlin, B. S.; Veige, A. S. Cyclic Polymers from Alkynes: Scope and Degradation. *Macromolecules* **2024**, *57* (1), 71−77.
(28) Jakhar, V. K.; Shen, Y. H.; Hyun, S. M.; Esper, A. M.; Ghiviriga, I.; Abboud, K. A.; Lester, D. W.; Veige, A. S. Improved Trianionic Pincer Ligand Synthesis for Cyclic Polymer Catalysts. *Organometallics* **2023**, *42* (12), 1339−1346.
(29) Shen, Y.-H.; Yadav, R.; Wong, A. J.; Balzer, A. H.; Epps, T. H.; Sumerlin, B. S.; Veige, A. S. Fibril size control, tensile strength, and electrical properties of cyclic polyacetylene. *React. Funct. Polym.* **2024**, *195*, 105810.
(30) Wang, T. W.; Huang, P. R.; Chow, J. L.; Kaminsky, W.; Golder, M. R. A Cyclic Ruthenium Benzylidene Initiator Platform Enhances Reactivity for Ring-Expansion Metathesis Polymerization. *J. Am. Chem. Soc.* **2021**, *143* (19), 7314−7319.
(31) Levenson, A. M.; Morrison, C. M.; Huang, P. R.; Wang, T. W.; Carter-Schwendler, Z.; Golder, M. R. Ancillary Ligand Lability Improves Control in Cyclic Ruthenium Benzylidene Initiated Ring-Expansion Metathesis Polymerizations. *ACS Macro Lett.* **2023**, *12* (10), 1286−1292.
(32) Jafari, M. G.; Russell, J. B.; Lee, H.; Pudasaini, B.; Pal, D.; Miao, Z.; Gau, M. R.; Carroll, P. J.; Sumerlin, B. S.; Veige, A. S.; et al. Vanadium Alkylidyne Initiated Cyclic Polymer Synthesis: The Importance of a Deprotiovanadacyclobutadiene Moiety. *J. Am. Chem. Soc.* **2024**, *146* (5), 2997−3009.
(33) Russell, J. B.; Konar, D.; Keller, T. M.; Gau, M. R.; Carroll, P. J.; Telser, J.; Lester, D. W.; Veige, A. S.; Sumerlin, B. S.; Mindiola, D. J. Metallacyclobuta-(2,3)-diene: A Bidentate Ligand for Stream-line Synthesis of First Row Transition Metal Catalysts for Cyclic Polymerization of Phenylacetylene. *Angew. Chem. Int. Ed.* **2024**, *63* (8), No. e202318956.
(34) Hurst, J. M.; Yadav, R.; Boeck, P. T.; Ghiviriga, I.; Brantley, C. L.; Dobrzycki, L.; Veige, A. S. Snapshot of cyclooctyne ring-opening to a tethered alkylidene cyclic polymer catalyst. *Chem. Sci.* **2024**, *15* (38), 15873−15879.
(35) Boeck, P. T.; Veige, A. S. Cyclic polymers from alkynes: a review. *Chem. Sci.* **2024**, *15*, 16006−16014.
(36) Aumann, R.; Heinen, H.; Kruger, C. Metal Template for the Symmetrical [2 + 2]-Dimerization of Ketenimines. *Angew. Chem. Int. Ed.* **1984**, *23* (3), 223−224.
(37) Mahlau, M.; Fernandes, R. A.; Brückner, R. First Synthesis of the Pyrano-Naphthoquinone Lactone (−)-Arizonin C1. *Eur. J. Org. Chem.* **2011**, *2011* (25), 4765−4772.
(38) Kretschik, O.; Heinz Dötz, K.; Nieger, M. Reactions of Complex Ligands, LXXII. Intermolecular Pauson-Khand Reactions of Ethyl 2-Phenylethynylcyclopropanecarboxylates and [Amino(trans-2-phenylethynylcyclopropyl)methylidene]pentacarbonylchromium(0). *Chem. Ber.* **1997**, *130* (4), 507−514.
(39) Buchert, M.; Reissig, H. U. Highly Functionalized Vinylcyclopropane Derivatives by Regioselective and Stereoselective Reactions of Fischer Carbene Complexes with 1,4-Disubstituted Electron-Deficient 1,3-Dienes. *Chem. Ber.* **1992**, *125* (12), 2723−2729.
(40) Aumann, R.; Trentmann, B. Organische Synthesen mit Übergangsmetallkomplexen, 53. 4-Methylencyclopentene und 5-Methylencyclohexenone aus "Fischer-Carbe"- Chromkomplexen, Allenen und Alkine. *Chem. Ber.* **1991**, *124* (10), 2335−2342.
(41) Wulff, W. D. 9.2 - Metal−Carbene Cycloadditions. In *Comprehensive Organic Synthesis*, Trost, B. M.; Fleming, I., Eds.; Pergamon, 1991; pp. 1065−1113.
(42) Merlic, C. A.; Burns, E. E. Chemoselectivity in the Isonitrile Metathesis Route to Aromatic-Amines. *Tetrahedron Lett.* **1993**, *34* (34), 5401−5404.
(43) Hoffmann, M.; Buchert, M.; Reissig, H. U. Reactions of Fischer carbene complexes with siloxydienes: Formation of cycloheptadiene and cyclopentene derivatives - Formal [2 + 1] cycloaddition followed by Cope rearrangement versus formal [3 + 2] cycloaddition with or without preceding carbene-ligand metathesis. *Chem.—Eur. J.* **1999**, *5* (3), 876−882.
(44) Barluenga, J.; Fañanás, F. J. Metalloxy Fischer carbene complexes: An efficient strategy to modulate their reactivity. *Tetrahedron* **2000**, *56* (27), 4597−4628.
(45) Barluenga, J.; Aznar, F.; Palomero, M. A. Easy and regioselective synthesis of highly functionalized o-quinodimethide precursors from Fischer carbene complexes and isocyanides. *Chem.—Eur. J.* **2002**, *8* (18), 4149−4163.
(46) Neidlein, R.; Gürtler, S.; Krieger, C. Chemische Reaktionen mit Fischer-Carben-Komplexen des 1,6-Methano[10]annulens. *Helv. Chim. Acta* **1994**, *77* (8), 2303−2322.
(47) Aumann, R.; Heinen, H. Organische Synthesen mit Übergangsmetall-Komplexen XLV. 3-Hydroxypyridine, 1H-Pyrrole und 2-Hydroxypyrrol-Derivate aus einem Aminocarben-Chromkomplex und Alkinen. *J. Organomet. Chem.* **1990**, *389* (1), c1−c6.
(48) Moderhack, D. Four-Membered Rings from Isocyanides-Recent Advances. *Synthesis* **1985**, *1985* (12), 1083−1096.
(49) Aumann, R.; Kuckert, E.; Heinen, H. 3-Aminoidoles, Imidazolidines, and Oxazolidines from Isocyanides and Carbene Complexes by Metal-Induced [4 + 2]- and [3 + 2]-Cycloadditions. *Angew. Chem., Int. Ed.* **1985**, *24* (11), 978−979.
(50) Leese, T.; Dötz, K. H. Reactions of Complex Ligands, LXX. An Intramolecular Alkyne Insertion/Carbonylation/Cyclization Sequence of Chromium Aminocarbene Complexes: A Novel Access to Indole and Indenoindole Skeletons. *Chem. Ber.* **1996**, *129* (6), 623−631.
(51) Aumann, R. Organische Synthesen mit Übergangsmetallkomplexen, 70. [2-(Galactopyranosylamino)ethenyl]carben- und 3-(Galactopyranosylamino)-1,2-propadienyliden-Komplexe durch 3-Addition von 2,3,4,6-Tetra-O-pivaloyl-β-D-galactopyranosylamin an Alkinylcarben-Komplexe (M = Cr, W). — Atropisomere Galactopyranosyl-Pyrrole durch Reaktion von 2-(Galactopyranosylamino)ethenyl]carben-Komplexen mit Isocyaniden. *Chem. Ber.* **1994**, *127* (4), 725−729.
(52) Fischer, H.; Troll, C. Verknüpfung von Cyanamiden mit einem Carbinliganden − Bildung von η^2-(C,N)-Imidazolium- und Ansa-Carben-Komplexen. *Chem. Ber.* **1993**, *126* (11), 2373−2378.
(53) Aumann, R. Organische Synthesen mit Übergangsmetall-Komplexen, 58. Heptafulvenylcarben-Komplexe von Chrom und Wolfram. − Azaspiro[4]-Anellierung an 1-Metalla-1,3-diene mit

https://doi.org/10.1021/acs.organomet.4c00442
Organometallics 2025, 44, 279−288

Isocyaniden; Liganden-Abspaltung mit Pyridin oder durch Thermolyse. *Chem. Ber.* **1992**, *125* (5), 1141−1145.
(54) Barluenga, J.; Aznar, F.; Palomero, M. A. Efficient synthesis of highly functionalized indazoles and 2,3-dihydro-1,2-benzisoxazoles by reaction of stable Fischer dienyl carbenes and isocyanides. *Chem.—Eur. J.* **2001**, *7* (24), 5318−5324.
(55) Barluenga, J.; Garcia-Rodriguez, J.; Martinez, S.; Suarez-Sobrino, A. L.; Tomas, M. Facile and versatile annulation of the imidazole ring: Single and sequential cyclization reactions of Fischer carbene complexes with 1,4-diazafulvenes. *Chem.—Eur. J.* **2006**, *12* (12), 3201−3210.
(56) Liu, J. Y.; Liu, X.; Wu, J. L.; Li, C. C. Total Synthesis of Natural Products Containing a Bridgehead Double Bond. *Chem* **2020**, *6* (3), 579−615.
(57) Bates, R. Carbene Complexes. In *Organic Synthesis Using Transition Metals*; John Wiley & Sons, Ltd, 2012; pp. 253−323.
(58) Roose, T. R.; Verdoorn, D. S.; Mampuys, P.; Ruijter, E.; Maes, B. U. W.; Orru, R. V. A. Transition metal-catalysed carbene- and nitrene transfer to carbon monoxide and isocyanides. *Chem. Soc. Rev.* **2022**, *51* (14), 5842−5877.
(59) Huang, J. Q.; Yu, M.; Yong, X.; Ho, C. Y. NHC-Ni(II)-catalyzed cyclopropene-isocyanide [5 + 1] benzannulation. *Nat. Commun.* **2022**, *13* (1), 4145.
(60) Fruhauf, H. W. Metal-Assisted Cycloaddition Reactions in Organotransition Metal Chemistry. *Chem. Rev.* **1997**, *97* (3), 523−596.
(61) Merlic, C. A.; Wu, F. Synthesis of β-keto Fischer carbene complexes. *J. Organomet. Chem.* **1998**, *553* (1−2), 183−191.
(62) Herndon, J. W. Applications of carbene complexes toward organic synthesis. *Coord. Chem. Rev.* **2000**, *206*, 237−262.
(63) Dötz, K. H.; Straub, W.; Ehlenz, R.; Peseke, K.; Meisel, R. Carbene Complex Functionalized Sugars. *Angew. Chem., Int. Ed.* **1995**, *34* (17), 1856−1858.
(64) Barluenga, J.; Santamaria, J.; Tomas, M. Synthesis of heterocycles via group VI Fischer carbene complexes. *Chem. Rev.* **2004**, *104* (5), 2259−2283.
(65) Barluenga, J.; Fernández-Rodríguez, M. A.; Aguilar, E. Group 6 Fischer carbene complexes: "chemical multitalents" for multicomponent reactions. *J. Organomet. Chem.* **2005**, *690* (3), 539−587.
(66) Aumann, R.; Krüger, C.; Goddard, R. Organische Synthesen mit Übergangsmetall-Komplexen, 59[1] Cyclobutanimine aus Carbenchrom- oder -wolfram-Komplexen, Isocyaniden und Alkenen durch 2 + 2]-Cycloadditionen intermediärer Ketenimin-Komplexe; Liganden-Abspaltung mit Pyridin. *Chem. Ber.* **1992**, *125* (7), 1627−1633.
(67) Grass, A.; Dewey, N. S.; Lord, R. L.; Groysman, S. Ketenimine Formation Catalyzed by a High-Valent Cobalt Carbene in Bulky Alkoxide Ligand Environment. *Organometallics* **2019**, *38* (4), 962−972.
(68) Liu, Z. H.; Cao, S. S.; Wu, J. Y.; Zanoni, G.; Sivaguru, P.; Bi, X. H. Palladium(II)-Catalyzed Cross-Coupling of Diazo Compounds and Isocyanides to Access Ketenimines. *ACS Catal.* **2020**, *10* (21), 12881−12887.
(69) Aumann, R.; Fischer, E. O. Transition Metal-Carbene Complexes, IV. Addition of Isonitriles to Methylmethoxycarbeneopentacarbonyl Chromium. *Chem. Ber.* **1968**, *101* (3), 954.
(70) Fryzuk, M. D.; Duval, P. B.; Mao, S. S. S. H.; Rettig, S. J.; Zaworotko, M. J.; MacGillivray, L. R. Reactivity Studies of the Zirconium Alkylidene Complexes $[\eta^5\text{-}C_5H_3\text{-}1,3\text{-}(SiMe_2CH_2PPr^{i2})_2]$-ZrCHR(Cl) (R = Ph, $SiMe_3$). *J. Am. Chem. Soc.* **1999**, *121* (8), 1707−1716.
(71) Basuli, F.; Bailey, B. C.; Watson, L. A.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. Four-coordinate titanium alkylidene complexes: Synthesis, reactivity, and kinetic studies involving the terminal neopentylidene functionality. *Organometallics* **2005**, *24* (8), 1886−1906.
(72) Mullins, S. M.; Bergman, R. G.; Arnold, J. Olefination and group transfer reactions of an electron deficient tantalum methylidene complex. *Dalton Trans.* **2006**, No. 1, 203−212.
(73) Yarrow, D. J.; Ibers, J. A.; Tatsuno, Y.; Otsuka, S. Structure and Mechanism of Formation of a Novel π-Bonded Ketenimine Complex, Bis(*tert*-butyl Isocyanide)(*N*-*tert*-butyldicyanoketenimine)nickel(0). Evidence for a Metal-Assisted Carbene Addition. *J. Am. Chem. Soc.* **1973**, *95* (26), 8590−8597.
(74) Cramer, R. E.; Panchanatheswaran, K.; Gilje, J. W. Isocyanide Insertion into a Uranium-Carbon Double Bond. *Angew. Chem., Int. Ed.* **1984**, *23* (11), 912−913.
(75) Sielisch, T.; Behrens, U. übergangsmetall-heteroallen-komplexe: XII. Synthese und struktur von bis (cyclopentadienyl)[η^2(C,N)-ketenimin]vanadium-komplexen. Strukturvergleich mit einem pentacarbonyl η^1 (N)-ketenimin] chrom-komplex. *J. Organomet. Chem.* **1986**, *310* (2), 179−187.
(76) Gallop, M. A.; Roper, W. R. Carbene and carbyne complexes of ruthenium, osmium, and iridium. In *Advances in organometallic chemistry*; Elsevier; 1986, Vol. *25*, pp. 121−198.
(77) Mitsudo, T.-A.; Watanabe, H.; Komiya, Y.; Watanabe, Y.; Takaegami, Y.; Nakatsu, K.; Kinoshita, K.; Miyagawa, Y. Synthesis, crystal structure and reactivities of the first η^4-vinylketenimine metal complexes. *J. Organomet. Chem.* **1980**, *190* (2), C39−C42.
(78) Aumann, R.; Heinen, H. Organische Synthesen mit Übergangsmetallkomplexen, 28. 3- und 4-Imino-2-azetidinone aus Isocyaniden und einem Mangan-Carbenkomplex. *Chem. Ber.* **1988**, *121* (6), 1085−1091.
(79) Aumann, R.; Meinen, H.; Krüger, C.; Tsay, Y.-H. Organische Synthesen mit Übergangsmetallkomplexen, 16. Ein neuer Weg zu δ-Carbolinen durch templatgesteuerte Mehrfachcyclisierung von Alkenyl-, Dienyl- sowie Thienylcarben-Komplexen mit Arylisocyaniden. *Chem. Ber.* **1986**, *119* (10), 3141−3149.
(80) Fernández, I.; Cossío, F. P.; Sierra, M. A. Mechanism of the Generation of Ketenimine−M(CO)n Complexes (M = Cr, W, Fe) from Fischer Carbenes and Isocyanides. *Organometallics* **2007**, *26* (12), 3010−3017.
(81) Aumann, R.; Althaus, S.; Krüger, C.; Betz, P. Organische Synthesen mit Übergangsmetallkomplexen, 33. 2-Azaallenyl-Chromkomplexe durch Kondensation von Aminocarben-Chromkomplexen mit Aldehyden, Säurechloriden oder-amiden. *Chem. Ber.* **1989**, *122* (2), 357−364.
(82) Moloy, K. G.; Fagan, P. J.; Manriquez, J. M.; Marks, T. J. A Synthetic and Mechanistic Study of Oxycarbene-Like Coupling Reaction Patterns of Actinide η^2-Acyl Complexes with Carbon-Monoxide and Isocyanides. *J. Am. Chem. Soc.* **1986**, *108* (1), 56−67.
(83) Cadierno, V.; Díez, J.; García-Álvarez, J.; Gimeno, J. (η^6-Arene)−Ruthenium(II) Complexes Containing Methanide and Methandiide Anions of $Ph_2P(=S)CH_2P(=NR)Ph_2$: Unprecedented Insertion of Isocyanide into a Ruthenium−Carbene Bond. *Organometallics* **2008**, *27* (8), 1809−1822.
(84) Cadierno, V.; García-Alvarez, J.; Gimeno, J.; Rubio-García, J. Reaction of isocyanides with iminophosphorane-based carbene ligands: Synthesis of unprecedented ketenimine-ruthenium complexes. *J. Organomet. Chem.* **2005**, *690* (24−25), 5856−5862.
(85) Li, J. H.; Kang, H. J.; Zhuo, K. Y.; Zhuo, Q. D.; Zhang, H.; Lin, Y. M.; Xia, H. P. Alternation of Metal-Bridged Metallacycle Skeletons: From Ruthenapentalyne to Ruthenapentalene and Ruthenaindene Derivative. *Chin. J. Chem.* **2018**, *36* (12), 1156−1160.
(86) Basuli, F.; Bailey, B. C.; Brown, D.; Tomaszewski, J.; Huffman, J. C.; Baik, M. H.; Mindiola, D. J. Terminal vanadium-neopentylidyne complexes and intramolecular cross-metathesis reactions to generate azametalacyclohexatrienes. *J. Am. Chem. Soc.* **2004**, *126* (34), 10506−10507.
(87) Adhikari, D.; Basuli, F.; Orlando, J. H.; Gao, X. F.; Huffman, J. C.; Pink, M.; Mindiola, D. J. Zwitterionic and Cationic Titanium and Vanadium Complexes Having Terminal M-C Multiple Bonds. The Role of the β-Diketiminate Ligand in Formation of Charge-Separated Species. *Organometallics* **2009**, *28* (14), 4115−4125.
(88) Russell, J. B.; Jafari, M. G.; Kim, J. H.; Pudasaini, B.; Ozarowski, A.; Telser, J.; Baik, M. H.; Mindiola, D. J. Ynamide and Azaalleneyl. Acid-Base Promoted Chelotropic and Spin-State Rearrangements in a

https://doi.org/10.1021/acs.organomet.4c00442
Organometallics 2025, 44, 279−288

Versatile Heterocumulene [(Ad)NCC(^{t}Bu)]$^-$. *Angew. Chem., Int. Ed.* **2024**, *63* (21), No. e202401433.
(89) Bailey, B. C.; Fan, H.; Baum, E. W.; Huffman, J. C.; Baik, M. H.; Mindiola, D. J. Intermolecular C-H bond activation promoted by a titanium alkylidyne. *J. Am. Chem. Soc.* **2005**, *127* (46), 16016−16017.
(90) Flores, J. A.; Cavaliere, V. N.; Buck, D.; Pintér, B.; Chen, G.; Crestani, M. G.; Baik, M. H.; Mindiola, D. J. Methane activation and exchange by titanium-carbon multiple bonds. *Chem. Sci.* **2011**, *2* (8), 1457−1462.
(91) Solowey, D. P.; Mane, M. V.; Kurogi, T.; Carroll, P. J.; Manor, B. C.; Baik, M. H.; Mindiola, D. J. A new and selective cycle for dehydrogenation of linear and cyclic alkanes under mild conditions using a base metal. *Nat. Chem.* **2017**, *9* (11), 1126−1132.
(92) Antinolo, A.; Fajardo, M.; Gilsanz, R.; Lopezmardomingo, C.; Otero, A.; Atmani, A.; Kubicki, M. M.; El Krami, S.; Mugnier, Y.; Mourad, Y. Synthesis, Structure, and Chemistry of Niobium Cationic Ketenimine Complexes, [Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-PhRCCNPh-C,N)-(L)]$^+$. Molecular Structure of [Nb(η^5-$C_5H_4SiMe_3$)$_2$(η^2-Ph_2CCNPh-C,N)(CH_3CN)][PF_6]. *Organometallics* **1994**, *13* (4), 1200−1207.
(93) Antinolo, A.; Fajardo, M.; Lopez Mardomingo, C.; Otero, A.; Mourad, Y.; Mugnier, Y.; Sanz-Aparicio, J.; Fonseca, I.; Florencio, F. Early-transition-metal ketenimine complexes. Synthesis, reactivity and structural characterization of complexes with η^2(C,N)-ketenimine groups bound to the halobis[(trimethylsilyl)cyclopentadienyl] niobium unit. X-ray structure of Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl(η^2(C,N)-PhN = C=CPh_2). *Organometallics* **1990**, *9* (11), 2919−2925.
(94) Bailey, B. C.; Fan, H.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. Room Temperature Ring-Opening Metathesis of Pyridines by a Transient Ti≡C Linkage. *J. Am. Chem. Soc.* **2006**, *128* (21), 6798−6799.
(95) Bailey, B. C.; Fout, A. R.; Fan, H.; Tomaszewski, J.; Huffman, J. C.; Gary, J. B.; Johnson, M. J.; Mindiola, D. J. Snapshots of an alkylidyne for nitride triple-bond metathesis. *J. Am. Chem. Soc.* **2007**, *129* (8), 2234−2235.
(96) Bailey, B. C.; Fan, H.; Huffman, J. C.; Baik, M.-H.; Mindiola, D. J. Intermolecular C−H Bond Activation Reactions Promoted by Transient Titanium Alkylidynes. Synthesis, Reactivity, Kinetic, and Theoretical Studies of the Ti≡C Linkage. *J. Am. Chem. Soc.* **2007**, *129* (28), 8781−8793.
(97) Figueroa, J. S.; Piro, N. A.; Mindiola, D. J.; Fickes, M. G.; Cummins, C. C. Niobaziridine Hydrides. *Organometallics* **2010**, *29* (21), 5215−5229.
(98) Feng, S. G.; White, P. S.; Templeton, J. L. Reactions of Vinyl Amido Ligands in Tp'$(CO)_2$W[N(R')CH = CHR] Complexes Prepared from Addition of Primary Amines to Coordinated Alkynes. *Organometallics* **1995**, *14* (11), 5184−5192.
(99) Bailey, B. C.; Huffman, J. C.; Mindiola, D. J.; Weng, W.; Ozerov, O. V. Remarkably stable titanium complexes containing terminal alkylidene, phosphinidene, and imide functionalities. *Organometallics* **2005**, *24* (7), 1390−1393.
(100) Elorriaga, D.; Carrillo-Hermosilla, F.; Antiñolo, A.; López-Solera, I.; Menot, B.; Fernández-Galán, R.; Villaseñor, E.; Otero, A. New Alkylimido Niobium Complexes Supported by Guanidinate Ligands: Synthesis, Characterization, and Migratory Insertion Reactions. *Organometallics* **2012**, *31* (5), 1840−1848.
(101) Beshouri, S. M.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. Observation of a facile isomerization of an early-transition-metal η^2-iminoacyl group via a 1,2-hydrogen shift. *Organometallics* **1987**, *6* (4), 891−893.
(102) Kurogi, T.; Miehlich, M. E.; Halter, D.; Mindiola, D. J. 1,2-CH Bond Activation of Pyridine across a Transient Titanium Alkylidene Radical and Re-Formation of the Ti = CH^{t}Bu Moiety. *Organometallics* **2018**, *37* (2), 165−167.
(103) Crestani, M. G.; Hickey, A. K.; Gao, X. F.; Pinter, B.; Cavaliere, V. N.; Ito, J. I.; Chen, C. H.; Mindiola, D. J. Room Temperature Dehydrogenation of Ethane, Propane, Linear Alkanes C4-C8, and Some Cyclic Alkanes by Titanium-Carbon Multiple Bonds. *J. Am. Chem. Soc.* **2013**, *135* (39), 14754−14767.
(104) Cavaliere, V. N.; Crestani, M. G.; Pinter, B.; Pink, M.; Chen, C. H.; Baik, M. H.; Mindiola, D. J. Room temperature dehydrogenation of ethane to ethylene. *J. Am. Chem. Soc.* **2011**, *133* (28), 10700−10703.
(105) Fout, A. R.; Scott, J.; Miller, D. L.; Bailey, B. C.; Pink, M.; Mindiola, D. J. Dehydrofluorination of Hydrofluorocarbons by Titanium Alkylidynes via Sequential C-H/C-F Bond Activation Reactions. A Synthetic, Structural, and Mechanistic Study of 1,2-CH Bond Addition and β-Fluoride Elimination. *Organometallics* **2009**, *28* (1), 331−347.
(106) Kurogi, T.; Carroll, P. J.; Mindiola, D. J. A radical coupled pathway to a stable and terminally bound titanium methylidene. *Chem. Commun.* **2017**, *53* (24), 3412−3414.
(107) Hickey, A. K.; Crestani, M. G.; Fout, A. R.; Gao, X.; Chen, C. H.; Mindiola, D. J. Dehydrogenation of hydrocarbons with metal-carbon multiple bonds and trapping of a titanium(II) intermediate. *Dalton Trans.* **2014**, *43* (26), 9834−9837.
(108) Crestani, M. G.; Olasz, A.; Pinter, B.; Bailey, B. C.; Fortier, S.; Gao, X. F.; Chen, C. H.; Baik, M. H.; Mindiola, D. J. Understanding the competitive dehydroalkoxylation and dehydrogenation of ethers with Ti-C multiple bonds. *Chem. Sci.* **2013**, *4* (6), 2543−2550.
(109) Reiß, F.; Reiß, M.; Bresien, J.; Spannenberg, A.; Jiao, H.; Baumann, W.; Arndt, P.; Beweries, T. 1-Titanacyclobuta-2,3-diene − an elusive four-membered cyclic allene. *Chem. Sci.* **2019**, *10* (20), 5319−5325.
(110) Levine, D. S.; Tilley, T. D.; Andersen, R. A. Evidence for the Existence of Group 3 Terminal Methylidene Complexes. *Organometallics* **2017**, *36* (1), 80−88.
(111) Grant, L. N.; Ahn, S.; Manor, B. C.; Baik, M. H.; Mindiola, D. J. Structural elucidation of a mononuclear titanium methylidene. *Chem. Commun.* **2017**, *53* (24), 3415−3417.
(112) Schrock, R. R. Alkylidene Complexes of Niobium and Tantalum. *Acc. Chem. Res.* **1979**, *12* (3), 98−104.
(113) Feldman, J.; Schrock, R. R. Recent Advances in the Chemistry of "d^0" Alkylidene and Metallacyclobutane Complexes. In *Progress in Inorganic Chemistry*, Lippard, S. J., Ed.; John Wiley & Sons, Inc, 1991, Vol. *39*, pp. 1−74.
(114) Mindiola, D. J.; Bailey, B. C.; Basuli, F. What a difference one electron makes!: Generating low-coordinate Ti-C and V-C multiply bonded frameworks through one electron oxidatively induced α-hydrogen abstractions. *Eur. J. Inorg. Chem.* **2006**, *2006* (16), 3135−3146.
(115) Wolczanski, P. T. Activation of Carbon-Hydrogen Bonds via 1,2-RH-Addition/-Elimination to Early Transition Metal Imides. *Organometallics* **2018**, *37* (4), 505−516.

https://doi.org/10.1021/acs.organomet.4c00442
Organometallics 2025, 44, 279−288