

# Vanadium Alkylidyne Initiated Cyclic Polymer Synthesis: The Importance of a Deprotiovanadacyclobutadiene Moiety

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**ABSTRACT:** Reported is the catalytic cyclic polymer synthesis by a 3d transition metal complex: a [V<sup>VI</sup>] alkylidyne, [(dBDI)V≡C<sup>t</sup>Bu(OEt<sub>2</sub>)] (**1-OEt<sub>2</sub>**), supported by the deprotonated β-diketiminato dBDI<sup>2-</sup> (dBDI<sup>2-</sup> = ArNC(CH<sub>3</sub>)CHC(CH<sub>2</sub>)NAr). Complex **1-OEt<sub>2</sub>** is a pre-catalyst for the polymerization of phenylacetylene to give cyclic polyphenylacetylene, whereas its precursor, complex [(BDI)V≡C<sup>t</sup>Bu(OTf)] (**2-OTf**; BDI<sup>-</sup> = [ArNC(CH<sub>3</sub>)<sub>2</sub>CH, Ar = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]) and the zwitterion [((C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B-dBDI)V≡C<sup>t</sup>Bu(OEt<sub>2</sub>)] (**3-OEt<sub>2</sub>**) exhibit low catalyst activity despite having the same alkylidyne ligand. Cyclic polymer topologies were verified by size-exclusion chromatography (SEC) and intrinsic viscosity studies. A component of the mechanism of the cyclic polymerization reaction was probed by isolation and full characterization of 4- and 6-membered metallacycles as model intermediates. Metallacyclobutadiene (MCBD) and deprotio-metallacyclobutadiene (dMCBD) complexes, (dBDI)V[C(<sup>t</sup>Bu)C(H)C(<sup>t</sup>Bu)] (**4-<sup>t</sup>Bu**) and (BDI)V[C(<sup>t</sup>Bu)CC(Mes)] (**5-Mes**), respectively, were synthesized upon reaction with bulkier alkynes, <sup>t</sup>Bu- and Mes-acetylene, with **1-OEt<sub>2</sub>**. Furthermore, the reaction of the conjugate acid of **1-OEt<sub>2</sub>**, (BDI)V≡C<sup>t</sup>Bu(OTf) (**2-OTf**), with the conjugated base of phenylacetylene, LiC≡CPh, yields the doubly deprotio-metallabenzene complex, [Li(THF)<sub>4</sub>]{(BDI)V[C(Ph)CC(<sup>t</sup>Bu)CC(Ph)]} (**6**). Protonation of the anionic 6-membered metallacycle **6**, yields **6-H<sup>+</sup>**, a catalytically active species towards the polymerization of phenylacetylene, for which the polymers were also confirmed to be cyclic by SEC studies. Computational mechanistic studies complement the experimental observations and provide insight into the mechanism of cyclic polymer growth. The non-innocence of the supporting dBDI<sup>2-</sup> ligand and its role in proton shuttling to generate deprotio-metallacyclobutadiene (dMCBD) complexes that proposedly culminate in the formation of catalytically active [V<sup>III</sup>] species is also discussed. This work demonstrates how a dMCBD moiety can react with terminal alkynes to form cyclic polymers.

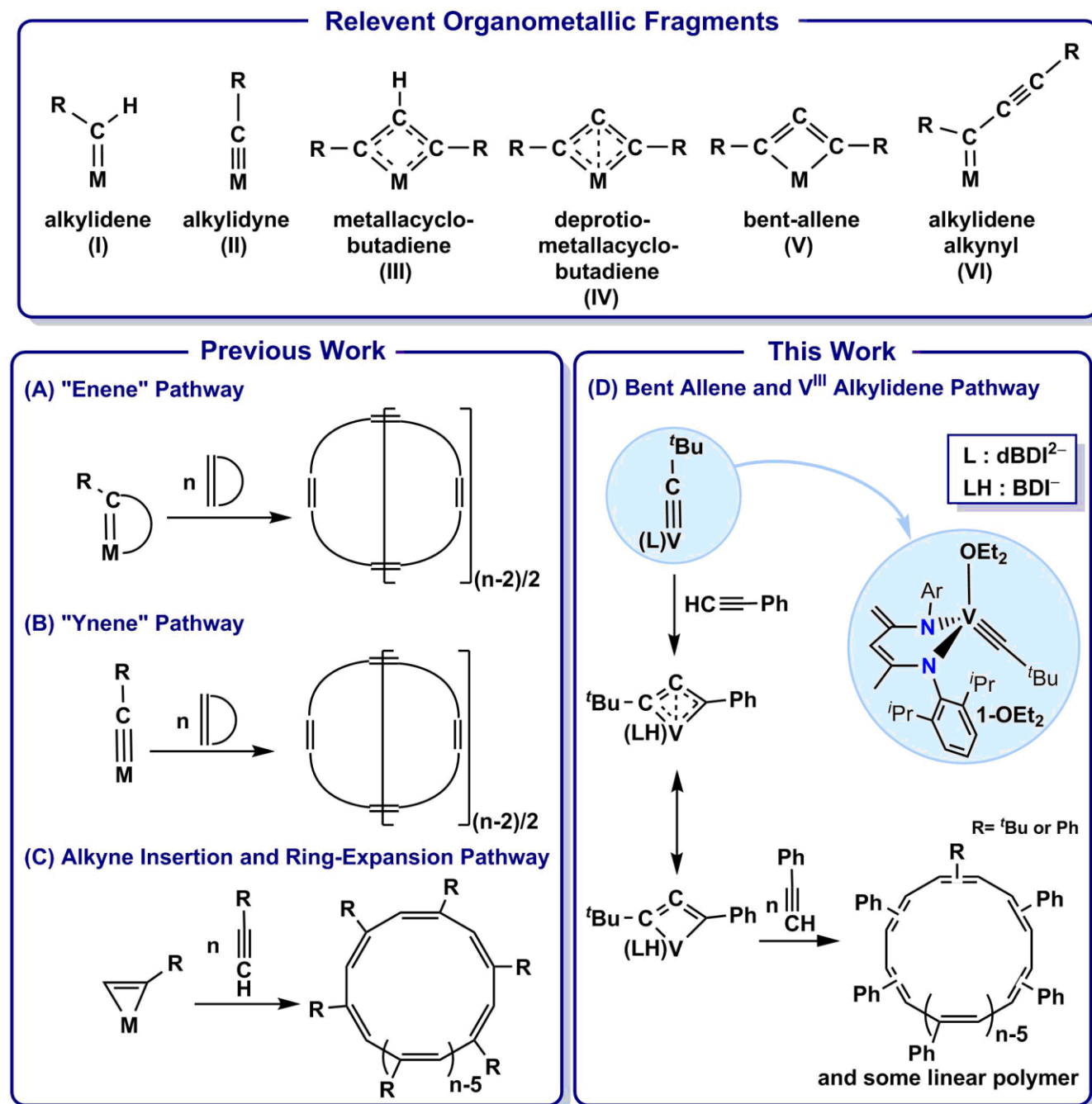
## INTRODUCTION

Polyalkynes are an important family of conjugated polymers known for their high and tunable electrical conductivity. These polymers possess not only excellent conductivity but also intriguing physical characteristics such as non-linear optical properties,<sup>1</sup> gas permeability,<sup>2</sup> and many other outstanding features. Consequently, they hold great promise for applications as organic conductive polymers,<sup>3</sup> optical limiters,<sup>1,4</sup> and membranes for gas separation.<sup>2</sup> Substituted polyacetylenes serve as substrates for synthesizing a diverse range of polymers through post-polymerization modifications.<sup>5</sup> Polymers with modified topologies offer potential advantages for fabricating specific materials and coatings, modifying surface properties, and facilitating drug delivery. Among these topologies, cyclic polymers are particularly interesting due to their unique properties arising from the absence of polymer chain termination points.<sup>4,6</sup> These “endless” and “continuous” polymers exhibit lower viscos-

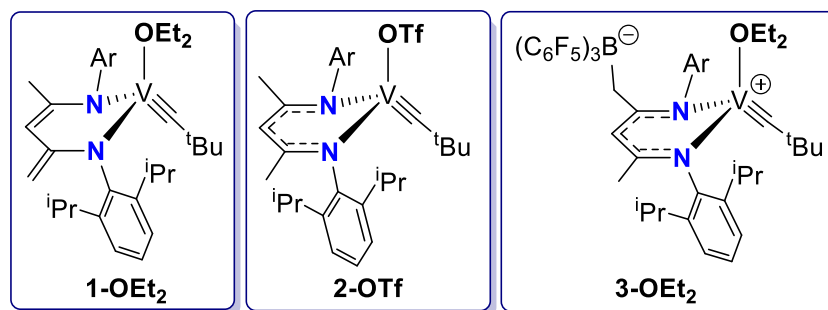
ity,<sup>7</sup> higher thermostability, shorter radii, smaller hydrodynamic volume,<sup>8</sup> higher refractive index, different reptation in solution media,<sup>9</sup> and distinctive surface properties.<sup>10,11</sup> Despite the excitement surrounding cyclic polymers, only a few reports described the polymerization of alkynes to access cyclic polyalkynes,<sup>12</sup> due to the challenging entropic penalties associated with their formation. Apart from the more traditional Ring-Closing Metathesis (RCM) methodology, which has its own challenges and drawbacks,<sup>13</sup> new methods developed by Grubbs, Veige, and co-workers established direct access to cyclic polyalkenes *via* the Ring Expansion Metathesis Polymerization (REMP), highlighted as Enene pathway in Scheme 1A.<sup>11, 14</sup> Veige and his team employed a [W<sup>VI</sup>] alkylidyne precursor and invoked an ynone mechanism to generate cyclic polynorbornene (Scheme 1B),<sup>15</sup> while Maeda and co-workers have shown that alkyne-adducts of Mo, W and Ta can also catalyze the cyclic polymerization of internal alkynes presumably *via* an insertion and ring-expansion pathway (Scheme 1C). However,

many aspects of these mechanisms remain to be fully understood.<sup>16</sup> Apart from these limited examples, a synthetic methodology for cyclic polymerization of alkynes using a 3d transition metal has yet to be established. Moreover, the

limited mechanistic information available for polymer growth hampers future catalyst design and optimization. In this work, we evaluate the catalytic activity of the only reported d<sup>0</sup> vanadium alkylidyne<sup>17</sup> for



Scheme 1. Top: Definitions for relevant organometallic fragments discussed in this work. Left: Cyclic polymerization involving the ring-expansion metathesis of a cyclic olefin with a tethered carbene (A, diene pathway), ring-expansion metathesis of a cyclic olefin with a carbyne (B, ynene pathway), or subsequent alkyne insertion using a metallacyclopropene (C, alkyne insertion and ring-expansion pathway). Right: Our study showing [2+2]-cycloaddition of a terminal alkyne with an alkylidyne followed by proton shuttling to form a bent allene which upon structural rearrangement and subsequent [2+2]-cycloadditions result in the formation of cyclic and linear polymer mixture (D).



**Figure 1.** [V<sup>V</sup>] Alkylidynes tested for polymerization of phenylacetylene (PA).

cyclic polymerization of phenylacetylene (PA) and present a comprehensive mechanistic investigation of how deprotono-metallacyclobutadienes (dMCBD) critically contribute to alkylidene formation and polymer propagation.

Scheme 1D presents a novel route for obtaining cyclic polymers of alkynes. The initiation step involves a [2+2]-cycloaddition of [M≡C] and [C≡C] bonds, followed by an unprecedented bimolecular deprotonation of the metallacycle. During this deprotonation process, the proton is transferred to the dBDI<sup>2-</sup> ligand (dBDI<sup>2-</sup> = ArNC(CH<sub>3</sub>)CHC(CH<sub>2</sub>)NAr, Ar = 2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). Experimental evidence is provided to illustrate how proton shuttling influences the reaction direction, thereby discouraging cycloreversion or alkyne cross-metathesis. The formation of a dMCBD (Scheme 1D) allows the vanadacycle to rearrange into a [V<sup>III</sup>] alkylidene with a pendant alkyne moiety. This

alkylidene-alkynyl species can then propagate *via* metathesis polymerization of PA. By preparing similar analogues of these metallacycles, including alternative routes to a pre-catalyst with a highly anionic 6-membered ring formed from the net fusion of two alkynes and the V≡C<sup>t</sup>Bu moiety (Compound 6), we demonstrate the likeliness of these intermediates participating in polymer initiation and propagation. Computational studies provide insights into the formation of dMCBD and its subsequent rearrangement to an alkylidene-alkynyl, which ultimately allows for the eventual formation of the cyclic poly(phenylacetylene) (*c*-PPA). This work represents the first systematic demonstration of how 3d transition metal-carbon multiple bonds can facilitate the formation of *c*-PPA.

**Table 1.1. Selected polymerization results.<sup>a</sup>**

Entry	[PhCCH]:[Cat.]	Cat.	[PhCCH] (M)	Reaction Time (h)	Reaction Volume (mL)	Conversion (%) <sup>b</sup>	$\bar{D}^c$	M <sub>n</sub> (kDa) <sup>c</sup>
1	100	1-OEt <sub>2</sub>	0.1	2	10	93	1.66	204
2	100	1-OEt <sub>2</sub>	0.2	2	5	94	1.30	172
3	1000	1-OEt <sub>2</sub>	0.2	2	10	15	-	-
4	1000	1-OEt <sub>2</sub>	0.2	4	10	21	1.80	181
5	1000	1-OEt <sub>2</sub>	0.2	6	10	44	1.32	197
6	1000	1-OEt <sub>2</sub>	0.4	6	5	62	1.48	140
7	1000	1-OEt <sub>2</sub>	1.0	6	2	72	2.02	133
8	1000	1-OEt <sub>2</sub>	0.2	12	10	69	1.48	93.5
9	1000	1-OEt <sub>2</sub>	0.4	12	5	89	1.60	82.5
10	1000	1-OEt <sub>2</sub>	1.0	12	2	94	1.64	62.9
11	100	2-OTf	0.5	20	2	23	-	-
12	500	3-OEt <sub>2</sub>	0.2	12	5	4	-	-
13	~1000	6-H <sup>+</sup>	0.4	12	5	19	1.49	115
14	~1000	6-H <sup>+</sup>	1.0	12	2	37	1.48	108
15	~10000	6-H <sup>+</sup>	1.8	12	2	8	-	-
16	~8362	6-H <sup>+</sup>	5.4	12	5	2	1.40	152.4

<sup>a</sup> All mentioned reactions have been performed in toluene and at room temperature. <sup>b</sup> Determined based on the mass of polymer after work-up. <sup>c</sup> Measured and determined by SEC analysis, calibrated by polystyrene standards.

## RESULTS AND DISCUSSION

### Polymerization Reactions and Polymer Topological Studies.

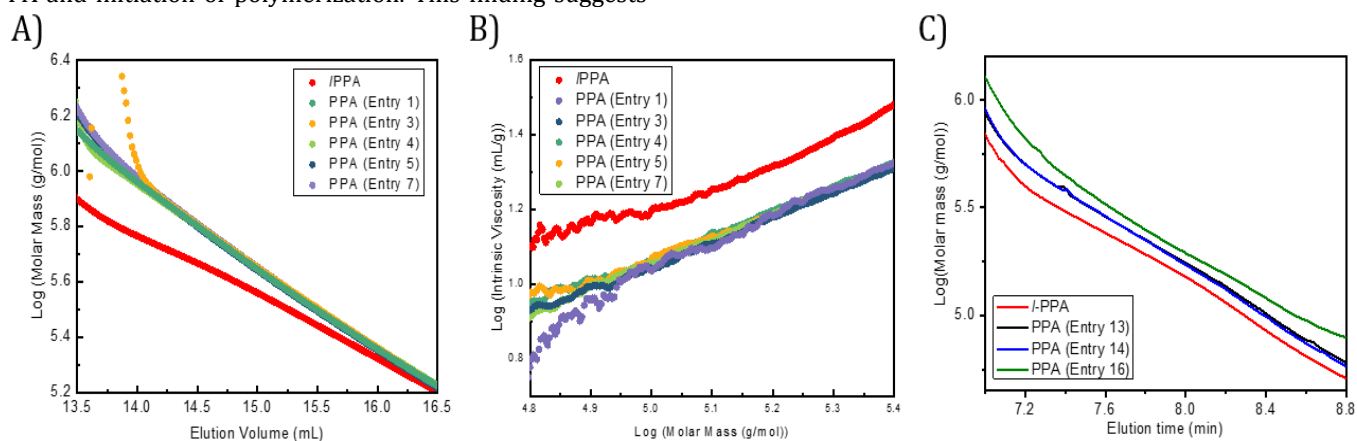
This study was motivated by previous findings in

2004, where complex **2-OTf**, in the presence of 1 equiv of  $\text{LiCH}_2\text{tBu}$ , polymerized PA to yield what was initially assumed to be linear poly(phenylacetylene), *l*-PPA.<sup>17a</sup> Considering the report by Veige et al., which demonstrated that an alkylidyne can initiate the polymerization of norbornene<sup>15</sup> and alkynes<sup>16c</sup> to give cyclic polymers, it seemed plausible to re-examine whether **2-OTf** could also be producing cyclic polymers. Thus, three [V<sup>V</sup>] alkylidynes (Figure 1) were tested for their activity in the polymerization of PA. Among these three species, **1-OEt<sub>2</sub>**, a [V<sup>V</sup>] alkylidyne complex bearing a deprotonated  $\beta$ -diketimate ( $\text{dBDI}^{2-}$ ) ligand, exhibited the highest yield and most promising reactivity for the polymerization of PA. Various reaction conditions with **1-OEt<sub>2</sub>** were screened (Table 1, entries 1–10), and it was determined that a 1:1000 ratio of [**1-OEt<sub>2</sub>**]:[PA] in toluene provides the best yield (94%) and rate (12 h) of polymers with a molecular weight ( $M_w$ ) in the order of  $10^5$  Da (entry 10). In comparison, catalyst **2-OTf** and **3-OEt<sub>2</sub>** offer yields below 25% and 5%, respectively, even with higher catalyst loadings (Table 1, entries 11 and 12). The higher reactivity of **1-OEt<sub>2</sub>** and **3-OEt<sub>2</sub>** can be attributed to the higher lability of  $\text{Et}_2\text{O}$  compared to triflate, as the elimination of  $\text{Et}_2\text{O}$  may facilitate the initial [2+2]-cycloaddition or activation of the alkyne and alkylidyne. Computational studies suggest that the dissociation of  $\text{Et}_2\text{O}$  requires about 20.7 kcal/mol of Gibbs free energy to form the transient and unsaturated [V]-complex  $[(\text{dBDI})\text{V}=\text{C}^t\text{Bu}] \{1\}$  with an open coordination site, as indicated by B3LYP calculations (Figure S20). The energy required is not prohibitive for subsequent coordination of PA and initiation of polymerization. This finding suggests

that weakly-coordinating solvents are optimal. Indeed, toluene exhibited the best solvent performance for these reactions, whereas coordinating solvents such as THF effectively halted the polymerization. Another observation from the polymerization studies is that more concentrated reaction conditions yield better results as long as the viscosity of the reaction media still allows for vigorous and effective stirring (Table 1, entries: 1 vs. 2, 5 vs. 6 vs. 7, and 8 vs. 9 vs. 10).

To compare the obtained polymers with the anticipated cyclic topology, linear analogs of poly(phenylacetylene) (*l*-PPA) were synthesized using (acac)Rh(COD) catalyst ( $\text{acac}^- = [\text{OC}(\text{CH}_3)_2\text{CH}]$ ).<sup>18</sup> The elution times of the PPA synthesized with **1-OEt<sub>2</sub>** catalyst and the standard *l*-PPA with similar molecular weights were compared by size-exclusion chromatography. The PPA prepared by **1-OEt<sub>2</sub>** catalyst exhibited longer elution times compared to the linear analogs, which is consistent with the presence of *c*-PPA. This is expected since the cyclic topology is anticipated to have a smaller hydrodynamic volume compared to its linear counterpart (Figure 2A, refer to Table 1 for reaction conditions). However, the convergence of elution volumes for lower molecular weights suggests the possibility of trace *l*-PPA impurities in the *c*-PPA sample.

Further evidence supporting the cyclic topology for polymers synthesized with catalyst **1-OEt<sub>2</sub>** is their lower intrinsic viscosities  $[\eta]$  throughout the molecular weight range compared to the linear analogs (Figure 2B).<sup>12a, 19</sup>



**Figure 2:** **A)** Log(molar mass) vs. elution volume for poly(phenylacetylene) samples (PPAs) (*c.f.* table 1 for reaction conditions). The red trace represents linear poly(phenylacetylene) prepared independently with (acac)Rh(COD) as the catalyst. **B)** Mark-Houwink-Sakurada plot for comparison of intrinsic viscosities over a wide range of molecular weights for linear and cyclic PPA (*l*-PPA and *c*-PPA) samples in THF at 35 °C. **C)** Log(molar mass) vs. elution volume of PPA synthesized with catalyst **6-H<sup>+</sup>** (*c.f.* table 1 for reaction conditions). The red trace represents *l*-PPA prepared independently with catalyst (acac)Rh(COD).

**Expected Reactivity of the Metal-Carbon Multiple Bond with Terminal Alkynes.** Cross-metathesis reactions involving transition metal alkylidynes with internal alkynes are well-known,<sup>20</sup> leading to the formation of a metallacyclobutadiene (MCBD) intermediate.<sup>21</sup> However when metal alkylidynes react with terminal alkynes, a different reaction occurs: [2+2]-cycloaddition followed by  $\beta$ -CH abstraction results in the formation of the corresponding dMCBD.<sup>20r, 22</sup> Interestingly, these dMCBD species initiate the formation of “unidentified” polymers through the expansion of the metallacyclic ring upon the addition of terminal alkynes.<sup>22a,</sup>

<sup>22c</sup> Since the initial reports on the formation of dMCBDs,<sup>22b</sup> there has been significant interest in their potential structural and electronic rearrangement to bent allenes and alkylidenes with pendent alkynyl groups.<sup>22c</sup> In 1993, Mortreux and coworkers proposed that dMCBD intermediates rearrange to form an alkylidene-alkynyl motif capable of initiating alkyne metathesis polymerization, resulting in the formation of polymers consisting of terminal alkynes.<sup>23</sup> However, the limited evidence for the polymerization mechanism from Schrock-alkylidynes and the insufficient

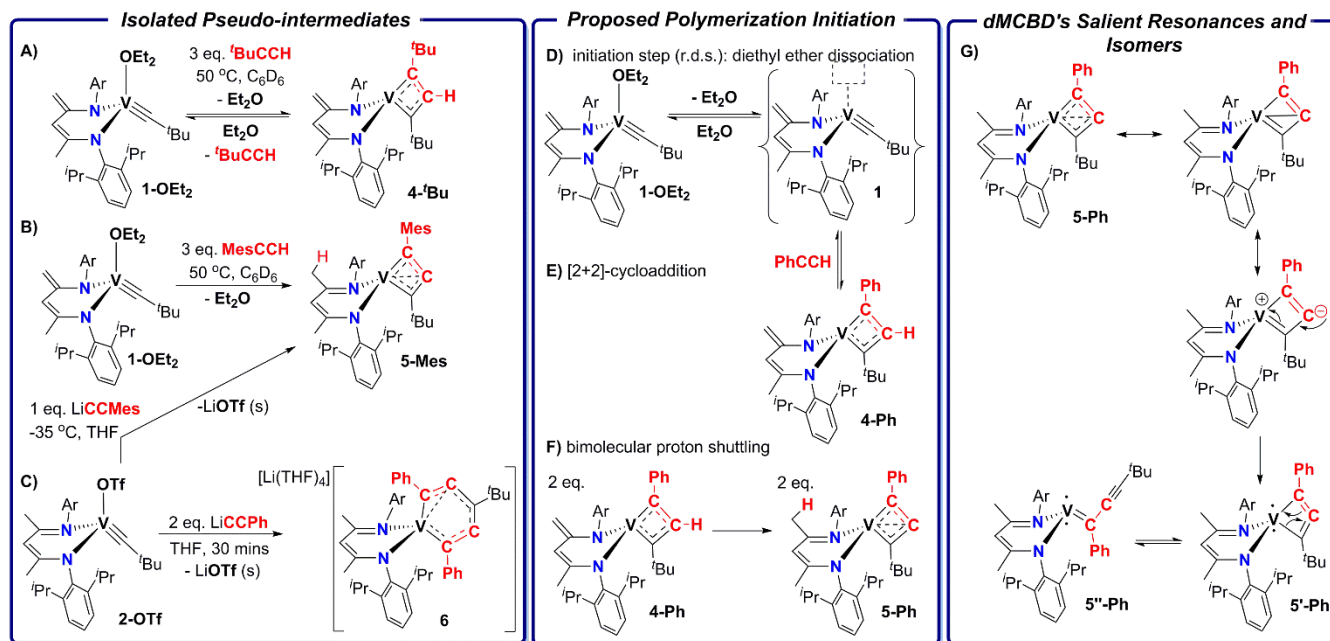
characterization of the resulting polymers have impeded the full realization of the potential of these catalysts.<sup>22a, 23-24</sup>

As mentioned above, dMCBD complexes are synthesized *via* [2+2]-cycloaddition of terminal alkynes with tungsten and molybdenum alkylidynes,<sup>20r, 22</sup> followed by irreversible deprotonation assisted by the ancillary ligand, often resulting in dissociation of the conjugate acid. In our case, when utilizing the V alkylidyne **1-OEt<sub>2</sub>** with a terminal alkyne such as phenylacetylene, we propose the formation of a similar MCBD species through [2+2]-cycloaddition, followed by deprotonation but without ligand dissociation. Such a transformation is possible since the dianionic supporting ligand (dBDI<sup>2-</sup>) has the potential to support the V complex as a monoanionic BDI<sup>-</sup> ligand after accepting a proton. To investigate the initiation steps, we examined the reactivity of **1-OEt<sub>2</sub>** with other terminal alkynes containing sterically congested groups: 1) an alkyl-substituted terminal alkyne with a less acidic terminal alkynyl CH group (<sup>t</sup>BuC≡CH) and 2) an aryl-substituted terminal alkyne with similar structure and terminal CH acidity to phenylacetylene (MesC≡CH). Using these substrates, the MCBD (**4-<sup>t</sup>Bu**) and dMCBD (**5-Mes**) species of V were isolated, which are of particular importance for understanding the polymerization mechanism and their unique compositions.<sup>21c, 25</sup> In this article, the labels **4-R** and **5-R** are used to denote putative or isolated MCBD and dMCBD species with various substitutions on the metallacycle, respectively, where R represents a <sup>t</sup>Bu, Mes, or Ph group.

**Mechanistic Studies on the Formation of Cyclic Polymers and the Isolation of Potential Catalytic Intermediates.** To investigate the initiation mechanism, we attempted to directly modulate the deprotonation of the MCPD inter-

mediate: the reaction of the V-alkylidyne and alkyne monomer *tert*-Butylacetylene (<sup>t</sup>BuC≡CH), containing a less acidic CH proton than PA, was chosen for this purpose. Treating complex **1-OEt<sub>2</sub>** with an excess of the <sup>t</sup>BuC≡CH in toluene over several hours did not result in polymer formation. However, when using 3 equivalents of <sup>t</sup>BuC≡CH in a toluene/benzene-*d*<sub>6</sub> mixture for 2 hours at 50 °C, the MCBD complex (dBDI)V[C(<sup>t</sup>Bu)C(H)C(<sup>t</sup>Bu)] (**4-<sup>t</sup>Bu**) was formed and isolated in 79% yield relative to **1-OEt<sub>2</sub>** (Scheme 2A). <sup>1</sup>H NMR spectral data of the reaction mixture indicate that complex **4-<sup>t</sup>Bu** is not formed quantitatively under these conditions and using a stoichiometric amount of the alkyne resulted in even lower yields.

Compound **4-<sup>t</sup>Bu** has two characteristic resonances in its <sup>1</sup>H NMR spectrum that correspond to the CH<sub>2</sub> fragment for the dBDI<sup>2-</sup> ligand backbone. These resonances appear at 3.01 and 3.74 ppm and are correlated to a single carbon negative contour at 81.5 ppm observable in a <sup>1</sup>H-<sup>13</sup>C{<sup>1</sup>H} HSQC experiment. Additional <sup>1</sup>H-<sup>13</sup>C{<sup>1</sup>H} HSQC and HMBC NMR spectroscopic experiments for **4-<sup>t</sup>Bu** reveal coupling of the β-CH (5.52 ppm) of the MCBD motif with the β-CH (96.4 ppm) and the α-C(<sup>t</sup>Bu) atoms of the MCBD framework (144.3 and 163.6 ppm). Furthermore, the asymmetric nature of the dBDI<sup>2-</sup> ligand results in the system being C<sub>1</sub> symmetric, with the methine and methyl groups of the <sup>i</sup>Pr moieties being magnetically inequivalent. The combination of these spectral data confirms the stability of the MCBD unit in complex **4-<sup>t</sup>Bu** and suggests that the unit does not undergo deprotonation or proton migration under the experimental conditions. Single-crystal X-ray diffraction (sc-XRD) analysis of **4-<sup>t</sup>Bu** (Figure 3A and 3E) reveals the diamond-like structure of the MCBD scaffold, with short V-C<sub>α</sub> (1.891(7) and 1.788(7) Å) and C<sub>α</sub>-C<sub>β</sub> distances (1.464(1) and

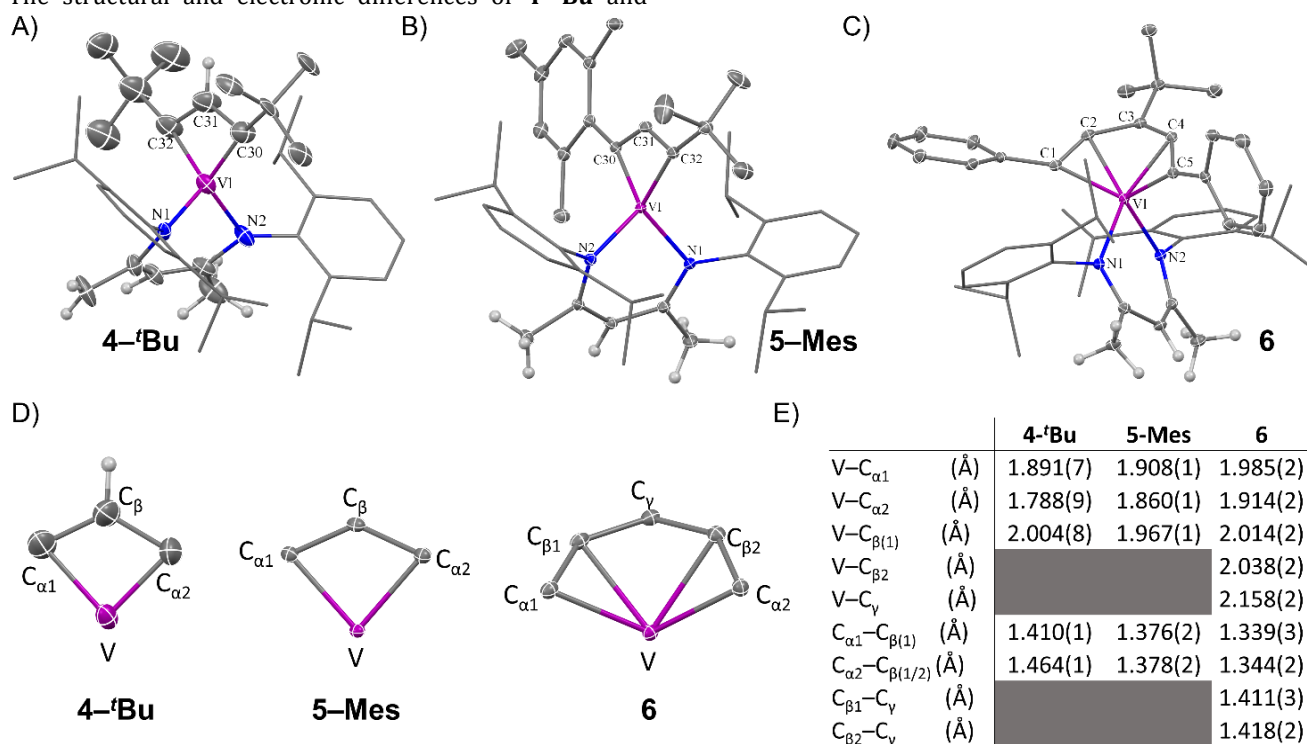


Scheme 2. Left: A) Synthesis of MCBD **4-<sup>t</sup>Bu** from **1-OEt<sub>2</sub>** and <sup>t</sup>BuC≡CH. B) Synthesis of the dMCBD **5-Mes** from **1-OEt<sub>2</sub>** and MesC≡CH. C) Synthesis of the six-membered metallacycle **6** *via* addition of 2 equiv of LiCCPh to **2-OTf**. Center: D) Dissociation of OEt<sub>2</sub> from **1-OEt<sub>2</sub>** followed by E) [2+2] cycloaddition of **1** and PA to form **4-Ph**. F) Bimolecular proton shuttling of **4-Ph** to yield **5-Ph**. G) Various resonance structures of **5-Ph** are shown, which can undergo structural change to afford a bent-allene (**5'-Ph**) or an alkyldiene-alkynyl species (**5''-Ph**).

1.410(1) Å). These features in the 4-membered ring indicate a more delocalized resonance structure for **4-<sup>t</sup>Bu**. Although the V–C<sub>β</sub> distance of 2.004(8) Å is shorter than the sum of their corresponding Van der Waals atomic radii (3.71 Å),<sup>26</sup> there are no orbital interactions between V and C<sub>β</sub> to suggest a strong covalent bond. The computed Mayer bond order of 0.32 between V and C<sub>β</sub> indicates the absence of a strong covalent bond between these atoms (Figure S21b).<sup>21c</sup> To further explore the reactivity of the V alkylidyne complex **1-OEt<sub>2</sub>**, the reaction with a more sterically hindered aryl alkyne, mesitylacetylene (MesCCH), was investigated (Table S1). MesCCH has a predicted pK<sub>a</sub> of 21.1, indicating its higher acidity compared to <sup>t</sup>BuCCH (pK<sub>a</sub> ~ 22.2, H<sub>2</sub>O, 25 °C; *calc.* 22.3)<sup>27</sup> and PA (pK<sub>a</sub> = 28.7, DMSO, 25 °C; *calc.* 20.3 in H<sub>2</sub>O).<sup>28</sup> Under the reaction conditions similar to those used for the formation of **4-<sup>t</sup>Bu**, treating **1-OEt<sub>2</sub>** with 3 equiv of MesCCH in toluene/benzene-*d*<sub>6</sub> at 50 °C did not yield a polymer. Instead, the complex (BDI)V[C(<sup>t</sup>Bu)CC(Mes)] (**5-Mes**) was isolated in 78% yield. Compound **5-Mes** lacks the characteristic CH<sub>2</sub> resonances of the dBDI<sup>2-</sup> ligand with no negative contour observed in the <sup>1</sup>H–<sup>13</sup>C{<sup>1</sup>H} HSQC NMR experiment. The absence of any sp<sup>2</sup> CH<sub>2</sub> group in **5-Mes** is further reflected in its C<sub>s</sub> symmetric nature, as evidenced by the presence of only one methyl resonance consistent with a BDI<sup>-</sup> ligand (<sup>1</sup>H NMR spectrum: 1.73 ppm). The <sup>13</sup>C{<sup>1</sup>H} DEPT–135 NMR spectrum of **5-Mes** further confirms the absence of methylene protons, indicating the protonation of dBDI<sup>2-</sup> to BDI<sup>-</sup> and the deprotonation of the MCBD in **5-Mes**. Moreover, the methyl and methine protons of the isopropyl groups exhibit four (0.22, 0.63, 1.41, and 1.50 ppm) and two (1.03 and 4.24 ppm) resonances, respectively, with <sup>3</sup>J<sub>H–H</sub> coupling constants of approximately 6.3 Hz, consistent with assigned C<sub>s</sub> symmetric nature of **5-Mes**. The structural and electronic differences of **4-<sup>t</sup>Bu** and

**5-Mes** are also reflected in their distinct <sup>51</sup>V NMR spectra, with resonances appearing at 251.6 and 1353.1 ppm for **4-<sup>t</sup>Bu** and **5-Mes**, respectively.

The sc-XRD data of **5-Mes** reveal two similar and relatively long V–C<sub>α</sub> distances (V–C(Mes): 1.908(1) Å, V–C(<sup>t</sup>Bu): 1.860(1) Å) in the dMCBD complex. The C<sub>α</sub>–C<sub>β</sub> distances (C(Mes)–C<sub>β</sub>: 1.376(2) Å, and C(<sup>t</sup>Bu)–C<sub>β</sub>: 1.378(2) Å) are comparable, indicating that the C(<sup>t</sup>Bu)CC(Mes) unit is bound to V as a formal 8e<sup>-</sup> donor and in an η<sup>3</sup>-fashion (Figure 3B and 3E). The V–C<sub>β</sub> distance of 1.967(1) Å is slightly shorter than that in **4-<sup>t</sup>Bu**, suggesting a stronger interaction between these atoms in **5-Mes** and indicating a more puckered structure for the metallacycle (Figure 3D). The C<sub>α</sub>–C<sub>β</sub>–C<sub>α</sub> angle in **5-Mes** is 131.71(1)°, which is more obtuse compared to **4-<sup>t</sup>Bu** (124.3(7)°) and similar to other structurally verified dMCBDs.<sup>23</sup> Based on the analogous acidities of MesCCH and PA, and considering the relative stability of compound **5-Mes**, it is possible that a similar dMCBD species, [(BDI)V[C(<sup>t</sup>Bu)CC(Ph)]] (**5-Ph**), initiates the polymerization of PA. Density functional theory (DFT) computations suggest that the Gibbs free energy of dMCBD is 10.2 (**5-<sup>t</sup>Bu**), 18.3 (**5-Mes**), and 13.7 kcal/mol (**5-Ph**), which are lower than their respective MCBD counterparts (Figure S21). It is proposed that the absence of the putative **5-<sup>t</sup>Bu** species experimentally observed is due to steric hindrance from adjacent tertiary butyl groups, preventing proton migration. The calculations indicate that the MCBD moiety in **5-Ph** is more fluxional and susceptible to a ring-opening mechanism compared to **5-Mes** (Figure S23). Additionally, it is demonstrated that the ring-opening mechanism plays a crucial role in enabling the coordination of PA monomers for the observed catalytic activity of the V species (*vide infra*).



**Figure 3:** Structural representation of **A)** **4-<sup>t</sup>Bu** with thermal ellipsoids at 30% probability level. **B)** **5-Mes** with thermal ellipsoids at 50% probability level. **C)** **6** with thermal ellipsoids at 50% probability level. Hydrogen atoms, except for those relevant to the discussion, disordered aryl, and <sup>t</sup>Bu groups in **4-<sup>t</sup>Bu**, co-crystallized hexane, and Li<sup>+</sup>(THF)<sub>4</sub> counter ion in **6**

are all omitted for clarity. Ar groups on the ligand are shown in capped stick style for simplicity. **D**) A closer structural demonstration of metallacyclic motifs and Greek alphabetical label assignments. **E**) Tabulated list of salient bond distances.

Interestingly, **5-Mes** can be independently obtained by using the conjugate acid of  $\text{dBDI}^{2-}$ , the  $\text{BDI}^-$  ligand framework, in combination with the conjugate base of  $\text{MesC}\equiv\text{CH}$ ,  $\text{LiC-Mes}$ . Specifically, a reaction between **2-OTf** and 1 equivalent of  $\text{LiCCMes}$  at  $-35^\circ\text{C}$  in THF affords **5-Mes** in 58% yield (Scheme 2B). In contrast, the addition of excess  $\text{}^t\text{BuC}\equiv\text{CH}$  or  $\text{MesC}\equiv\text{CH}$  to complex **2-OTf** does not induce [2+2]-cycloaddition even at elevated temperatures, but rather leads to decomposition of **2-OTf** as observed  $^1\text{H}$  NMR spectroscopy. Based on this difference in reactivity of **1-OEt<sub>2</sub>** and **2-OTf** in cycloaddition reactions with alkynes, it is hypothesized that the dissociation of  $\text{OEt}_2$  from **1-OEt<sub>2</sub>** is crucial for the cycloaddition of terminal alkyne to occur. This stark difference in reactivity between alkynes and **1-OEt<sub>2</sub>** and **2-OTf** provides a hypothesis for the difference in polymerization activity and mechanism for initiation. Complex **1-OEt<sub>2</sub>** contains a site for protonation and readily facilitates proton transfer to form the dMCBD intermediate, which can then accept additional alkyne monomer units. On the other hand, the  $\text{BDI}^-$  ligand  $\text{V}$ -alkylidyne **2-OTf** cannot accept a proton, thus preventing access to the dMCBD intermediate.

To further investigate the hypothesis of dMCBD participation *via* proton transfer, the respective conjugate acid-base pairs of **1-OEt<sub>2</sub>** and PA were examined. Treating **2-OTf** with 2 equivalents of  $\text{LiCCPh}$  at  $-35^\circ\text{C}$  in THF resulted in the formation of a new compound in nearly quantitative yield (93% isolated yield). The verified structural identity of the complex is a doubly deprotonated metallabenzene ate complex with a  $\text{BDI}^-$  ligand,  $[\text{Li}(\text{THF})_4][[\text{BDI}]\text{V}\{\text{C}(\text{Ph})\text{CC}(\text{}^t\text{Bu})\text{CC}(\text{Ph})\}]$  (**6**) (Scheme 3). The use of stoichiometric amounts of  $\text{LiCCPh}$  yields **6** with unreacted **2-OTf**. The isolation of complex **6** tantalizingly suggests that proton shuttling between the supporting ligand, the alkyne, and the MCBD intermediate is necessary for the expansion of the vanadacycle. In contrast, combining **1-OEt<sub>2</sub>** and  $\text{LiCCPh}$  did not result in any reaction even when the mixture was heated to  $50^\circ\text{C}$ .

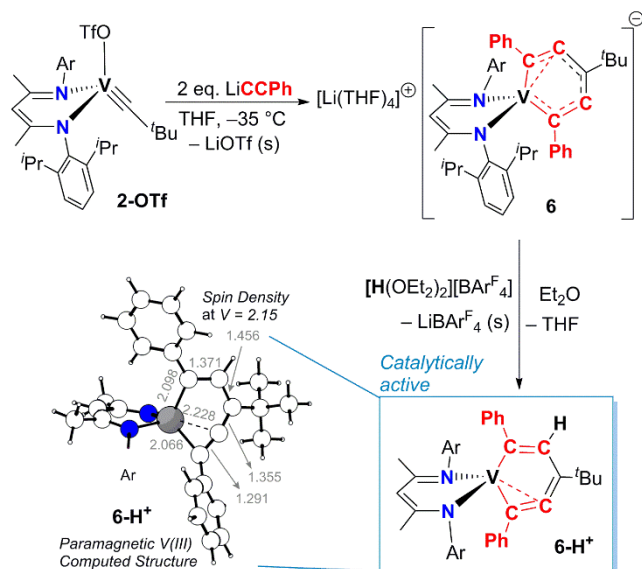
Compound **6** was characterized using multinuclear and multidimensional NMR spectroscopy and *sc*-XRD. In the  $^1\text{H}$  NMR spectrum, the characteristic resonance of the methine  $\gamma\text{-CH}$  group in the ring of the  $\text{BDI}^-$  ligand was observed at 5.76 ppm, which correlated to a carbon resonance at 97.41 ppm in the  $^1\text{H}\text{-}^{13}\text{C}\{\text{}^1\text{H}\}$  HSQC NMR spectrum. The methyl groups of the  $\text{BDI}^-$   $\beta$ -carbons appeared as two separate resonances in both the  $^1\text{H}$  and  $^{13}\text{C}\{\text{}^1\text{H}\}$  NMR spectra ([1.60, 24.44] and [2.17, 25.65] ppm), indicating the lack of a mirror plane in complex **6** ( $C_1$  symmetry). The methine (2.08, 3.18, 3.74, and 3.94 ppm) and methyl ( $-0.03$ , 1.09, 1.38, and 1.49 ppm) resonances of the  $^i\text{Pr}$  moieties, exhibiting  $^3J_{\text{HH}}$  coupling constants of  $\sim 5.2$  Hz, further confirmed the  $C_1$  symmetric nature of the compound.

Single crystals of **6** suitable for *sc*-XRD study were obtained from a THF/hexane diffusion at  $-35^\circ\text{C}$ . The solid-state structure belongs to a monoclinic and centrosymmetric  $P2_1/n$  space group. The structure reveals that the  $\text{V-C}_\alpha$  bonds (1.914(2) and 1.985(2) Å) are longer than the respective bonds found in both **4-<sup>t</sup>Bu** and **5-Mes** (Figure 3E), indicative of the interaction between  $\text{V}$  and all carbons composing the doubly deprotonated metallabenzene. The  $\text{V-C}_\beta$

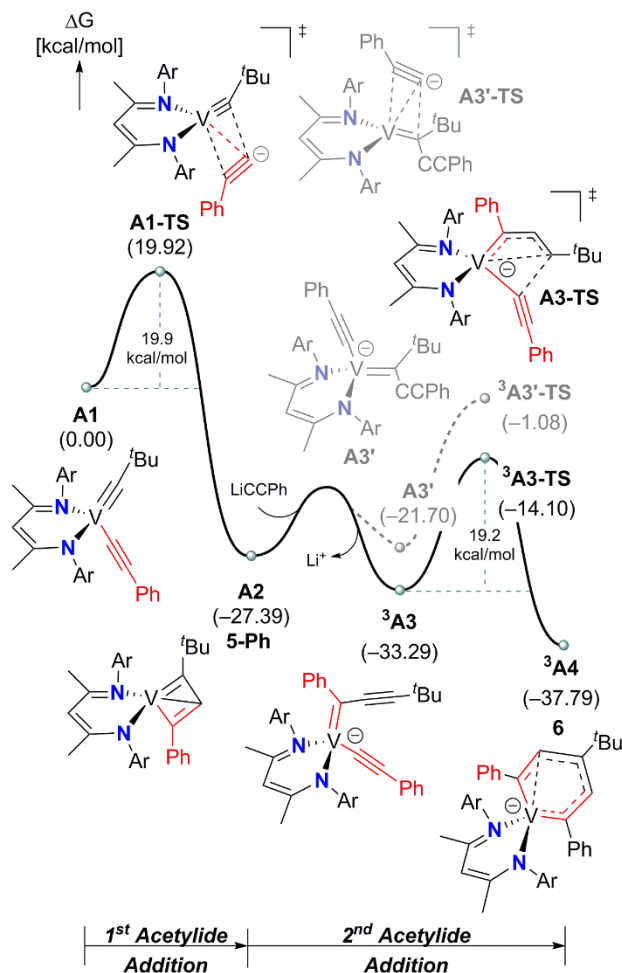
bond distances (2.038(2) and 2.014(2) Å) and  $\text{V-C}_\gamma$  bond distance of 2.158(2) Å are all shorter than the sum of van der Waals radii. The  $\text{C}_5\text{R}_3$  motif ( $\text{R} = \text{}^t\text{Bu}$  and two Ph) is a penta-anionic ligand ( $10e^-$  donor) bound to the  $[\text{V}^{\text{V}}]$  center in an  $\eta^5$  fashion, creating a Hückel aromatic system. The  $\text{V}$  center dips below the  $\text{C}_5$  ring by  $\sim 1.03$  Å, exhibiting a structural non-planarity similar to the slippage of metal centers observed in most metallabenzenes.<sup>29</sup> Upon closer inspection, the five carbons representing the  $\text{C}_5\text{R}_3$  fragment were found to be nearly planar, with the  $\beta$ -carbons slightly puckered by 0.093 Å and 0.193 Å from the imaginary plane composing the  $\text{C}_\alpha\text{C}_\gamma\text{C}_\alpha$  atoms. The phenyl groups on the  $\alpha$ -carbons deviate slightly from being orthogonal ( $74.5(4)^\circ$ ), and the plane of the two aryl groups on the  $\beta$ -diketimate make an angle of  $35.1(3)^\circ$ , indicating the absence of notable symmetry elements in **6** (Figure 3C).

**Route to Cyclic Polymers of PA Using Precursor 6.** The formation of complex **6** from **2-OTf** and  $\text{LiCCPh}$  can shed light on the role of the  $\text{BDI}^-$  ligand. Figure 4 presents a proposed mechanism for the formation of complex **6**, which incorporated DFT calculations and experimental observations. The reaction begins with the displacement of triflate by acetylide to form **A1**, accompanied by the precipitation of  $\text{LiOTf}$  (observed experimentally). Transition state **A1-TS**, representing a [2+2] cycloaddition typical of alkyne metathesis,<sup>21c</sup> leads to intermediate **5-Ph**. The barrier associated with **A1-TS** is 19.9 kcal/mol and intermediate **5-Ph** releases  $-27.4$  kcal/mol of free energy.

The second addition of  $\text{LiCCPh}$  occurs on the triplet electronic surface. Scheme 2G (vide supra) illustrates the plausible mechanism of electronic reorganization of **5-Ph** to a ring-opened intermediate **5''-Ph**, which allows for the coordination of  $\text{-CCPh}$  and the formation of intermediate **A3**. In the presence of excess  $\text{LiCCPh}$ , the formation of **A3** is energetically preferred by 5.9 kcal/mol. Subsequently, intermediate **A3** undergoes a cyclization reaction to transform into complex **6**, as illustrated in Figure 4. This step traverses the transition state **A3-TS**, which is characterized as an alkynyl group transfer to the terminal end of the growing metallacycle fragment. Notably, the second addition of  $\text{-CCPh}$  does not proceed through an  $\eta^2$ -type transition state, **<sup>3</sup>A3'-TS**, because the reaction pathway requires the isomerization to an 11.6 kcal/mol higher energy isomer **<sup>3</sup>A3'**, resulting in a barrier of 32.2 kcal/mol for this step. In comparison, the calculated barrier for the second acetylide addition *via* transition state **<sup>3</sup>A3-TS** is 19.2 kcal/mol. Furthermore, this barrier is 0.7 kcal/mol lower than the barrier for the first acetylide addition that leads to the formation of **5-Ph** (Figure 4). The implication of the lower barrier for the second  $\text{LiCCPh}$  addition is that the isolation of **5-Ph** under these reaction conditions is unlikely.



**Scheme 3.** Pathway to metallacycle species **6** and **6-H<sup>+</sup>**. [BAR<sup>F</sup><sub>4</sub>]<sup>-</sup> = [B(C<sub>6</sub>H<sub>3</sub>(3,5-CF<sub>3</sub>)<sub>2</sub>)<sub>4</sub>]<sup>-</sup>, Ar = 2,6-DIPP along with the computed structure for catalytically active **6-H<sup>+</sup>**. Distances are reported in Angstroms.

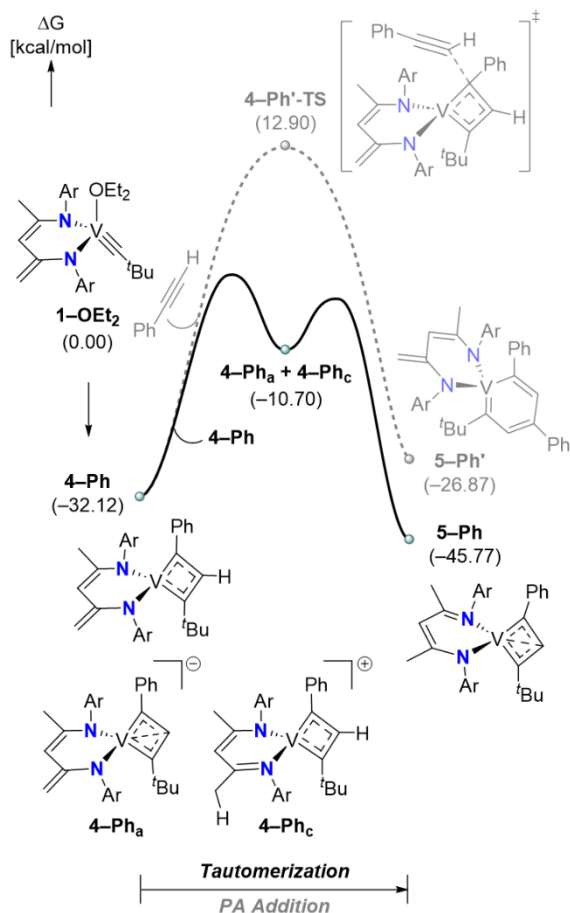


**Figure 4.** Proposed mechanism for the formation of **6**. Computational Method: B3LYP-D3/LACVP3P/cc-pVTZ(-f)//B3LYP-D3/LACVP/6-31G\*\* with entropic contributions at -35 °C. Ar = 2,6-DIPP.

Complex **6** is inactive in polymerizing PA. However, the activity of its conjugate acid, **6-H<sup>+</sup>**, in the formation of *c*-PPA was demonstrated by introducing a suitable proton source with a weakly coordinating anion. We hypothesized that neutralization of **6** with a H<sup>+</sup> would form a catalytically active species since its composition would be equivalent to **5-Ph** and PA. The addition of 1 equivalent of Brookhart's acid, [H(OEt<sub>2</sub>)<sub>2</sub>][BAR<sup>F</sup><sub>24</sub>] ([BAR<sup>F</sup><sub>4</sub>]<sup>-</sup> = [B(C<sub>6</sub>H<sub>3</sub>(3,5-CF<sub>3</sub>)<sub>2</sub>)<sub>4</sub>]<sup>-</sup>),<sup>30</sup> to **6** at -35 °C in diethyl ether resulted in an immediate color change from cherry-red to brown. After workup and removal of [Li][BAR<sup>F</sup><sub>24</sub>] and volatiles, a paramagnetic complex was obtained, as indicated by its broad resonances spanning from -32 to 22 ppm in the <sup>1</sup>H NMR spectrum. Despite several attempts, the species which we propose to be (BDI)V{C(Ph)CHC(<sup>t</sup>Bu)CC(Ph)} (**6-H<sup>+</sup>**) could not be crystallized. Based on the proposed formation of **6-H<sup>+</sup>** in Scheme 3, a solution magnetic moment susceptibility measurement was conducted using the Evans method, and this revealed a magnetic moment μ<sub>eff</sub> = 2.71 μ<sub>B</sub> (in C<sub>6</sub>D<sub>6</sub>, 300 K), consistent with a [V<sup>III</sup>]-d<sup>2</sup> high-spin system. Computational studies suggest that **6-H<sup>+</sup>** is most stable in the triplet state with a Mulliken spin density of 2.15, which is suggestive of a high-spin [V<sup>III</sup>] center with two d-orbital based valence electrons and some additional spin densities gained from the highly polarizable ligands, as depicted in Scheme 3.

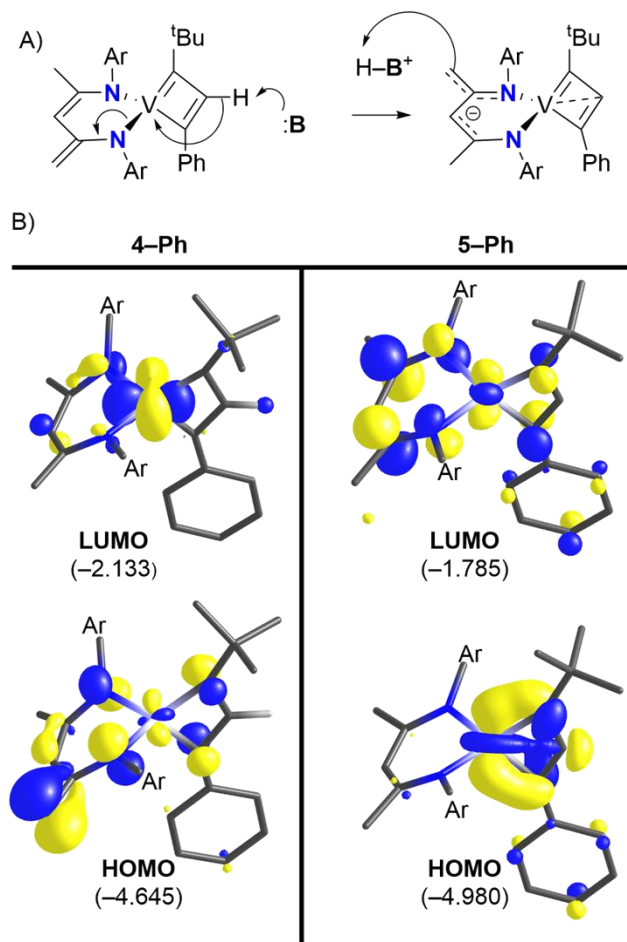
Complex **6-H<sup>+</sup>** was found to be active in catalyzing the polymerization of PA, resulting in the synthesis of cyclic poly(phenylacetylene), *c*-PPA. The polymer products obtained using **6-H<sup>+</sup>** exhibit a longer elution time compared to their linear counterparts. This observation is consistent with the anticipated cyclic topology of *c*-PPA. The plot of log(molar mass) vs. elution time demonstrates the difference in elution times between the synthesized polymers and linear poly(phenylacetylene) (*l*-PPA), further supporting their cyclic nature (Figure 2C, and Table 1 entries 13–15 for reaction conditions). The SEC (size-exclusion chromatography) data indicates that the elution times of *c*-PPA synthesized using catalyst **6-H<sup>+</sup>** do not overlap with those of *l*-PPA in the lower molar mass range. This suggests that the *c*-PPA obtained using **6-H<sup>+</sup>** has fewer linear impurities compared to the *c*-PPA synthesized with catalyst **1-OEt<sub>2</sub>** (Figure 2C and Table 1). It should be noted that while complex **6-H<sup>+</sup>** is active in catalyzing the polymerization of PA, its activity is lower compared to **1-OEt<sub>2</sub>**. However, the SEC data still confirms the successful synthesis of *c*-PPA with reduced amounts of linear impurities using catalyst **6-H<sup>+</sup>**.





**Figure 5.** Tautomerization vs. PA addition from **4-Ph**. Computational Method: B3LYP-D3/ LACV3P/cc-pVTZ(-f)/B3LYP-D3/ LACVP/6-31G\*\* with entropic contributions at 25 °C.

**Proton Transfer to Form the dMCBD Scaffold in 5-Mes and Putative 5-Ph.** The rearrangement of the MCBD scaffold to a dMCBD in complex **5-Mes** and the proposed **5-Ph** intermediate (Schemes 2B and 2F) raises questions about the mechanism of this transformation and the role of the BDI ligand in the polymerization. Similarly, the ability of **6-H<sup>+</sup>** to catalyze the polymerization of PA into *c*-PPA suggests that an analogous intermediate with a BDI ligand may appear during the initial stages of polymerization when precatalyst **1-OEt<sub>2</sub>** is used. To gain insight into these key mechanistic features, DFT calculations were performed starting from the presumed **4-Ph** structure formed upon the [2+2] cycloaddition of PA to the alkylidyne ligand in **1-OEt<sub>2</sub>** (Figure S20).



**Figure 6. A)** Proposed mechanism for the tautomerization with the assistance of an external base. **B)** Kohn-Sham orbitals, with isodensity values of 0.5 a.u., illustrate electronic reorganization due to tautomerization. Values in parenthesis are the orbital energies in eV (Ar = 2,6-DIPP).

Calculations indicate that the intermediate **4-Ph** may not undergo the subsequent PA addition step under the given reaction conditions. The calculated barrier for the PA addition to form a 6-membered vanadacycle intermediate, **5-Ph<sup>\*</sup>**, is 45.0 kcal/mol, much too high for a reaction performed at room temperature. The main reason for this high barrier is the lack of access of the PA monomer to the vanadium center. The transition state of this outer-sphere mechanism involves the electrophilic addition of PA to the C<sub>α</sub> of the cyclobutadiene without any assistance by the V-center (Figure 5).

The mandatory addition of H<sup>+</sup> to the dBDI<sup>2-</sup> backbone to form **5-Mes** and the intermediate **5-Ph**, demands that the MCBD resulting from [2+2] cycloaddition of the terminal alkyne must relinquish a proton to the dBDI<sup>2-</sup> ligand. This tautomerization can be envisioned to proceed with the assistance of an external base, as illustrated in Figure 6A. Because the mechanistic role of such a base is to simply act as a proton shuttle, even **4-Ph** itself is a viable candidate. In this scenario, tautomerization could involve a bimolecular process where two molecules of **4-Ph** exchange proton and transform into the corresponding conjugate acid-base pairs (dBDI)V[C(Ph)CC(Ph)] (**4-Ph<sub>a</sub>**) and (BDI)V[C(Ph)CHC(Ph)]

(**4-Ph<sub>c</sub>**). These ion pairs can then combine and neutralize through a second proton exchange, leading to the formation of two equivalents of **5-Ph** and release 35.1 kcal/mol of Gibbs free energy. The deprotonated form, **5-Ph**, is thermodynamically favored by 13.7 kcal/mol over the protonated form, *e.g.*, **4-Ph** (Figure 5). Thus, the self-promoted tautomerization is thermodynamically favorable.

Our calculations show that the proton shuttling causes an electronic reorganization that significantly impacts the chemical reactivity. As illustrated in Figure 6B, the HOMO in **4-Ph** is delocalized over the BDI<sup>-</sup> ligand, whereas the LUMO features a non-bonding, in-plane *d*-orbital at vanadium, consistent with a [V<sup>V</sup>] d<sup>0</sup> complex in which all non-bonding and M-L anti-bonding frontier orbitals are expected to be empty. During the tautomerization, the positive charge associated with the addition of the proton lowers the energies of all BDI-based orbitals, while the energies of orbitals located at the MCBBD-fragment increase due to the newly created negative charge associated with the proton loss at that site. The result of these energy shifts is that one of the BDI-based π\*-orbitals that was higher in energy than the metal-based LUMO in **4-Ph** becomes the LUMO in **5-Ph**. Likewise, the HOMO in **5-Ph** is one of the V-C σ-bonding orbitals that houses the valence electrons responsible for the σ-bonding interactions in the dMCBD moiety (Figure 6B). It is important to distinguish that the proton-transfer is not associated with any redox event and the oxidation states of the metal and ligands remain unchanged, *i.e.* the vanadium center maintains a formal [V<sup>V</sup>] oxidation state in both species.

The elevation of the orbital responsible for maintaining the V-C σ-bonding framework in the MCBBD fragment to the HOMO level weakens the metallacycle and gives access to a bent-alkene complex **5'-Ph** and also an alkylidene-alkynyl species (**5''-Ph**), which is formed through a formal reductive elimination and, thus, features a [V<sup>III</sup>]-center, as highlighted in Scheme 2G. Similar rearrangements were only speculated upon by Mortreux and co-workers in the formation of topologically undefined polymeric material from terminal alkynes and Schrock carbynes.<sup>23</sup> Although the precise identity of the active state of the catalyst remains unclear, these rearrangements are plausible. It is also notable that the UV-Vis spectrum of **5-Mes** features absorptions in the visible range with ε values in the range of 170 – 210 M<sup>-1</sup> cm<sup>-1</sup>, which may be assigned to be a d-d transition that are reasonable for a [V<sup>III</sup>] intermediate.

## CONCLUSIONS

In conclusion, this work demonstrates for the first time that 3d transition metal alkylidyne such as **1-OEt<sub>2</sub>** can polymerize PA and emphasizes the crucial role of ancillary ligands in the catalytic process. The polymers produced using these vanadium catalysts were found to be predominantly cyclic, showcasing the potential of this catalytic system for targeting interesting polymer morphologies. By exploring the reaction of the conjugate acid of the vanadium alkylidyne, **1-OTf**, with the conjugate base of PA, -CCPh, we identified and characterized the doubly-deprotonated vanadabenzene ate complex, **6**. Upon protonation, this complex yields a neutral and paramagnetic complex, **6-H<sup>+</sup>**, which exhibits catalytic activity for the polymerization of PA, resulting in cyclic polymers with minimal linear impurities.

The mechanism of vanadium-alkylidyne catalyzed cyclic polymer formation from alkynes is still under investigation, but this work provides initial insights into the early stages of the reaction and the role of the dMCBD scaffold. Evidence supports the initiation of the polymerization through [2+2]-cycloaddition, as observed by the isolation of **4-<sup>t</sup>Bu** from **1-OEt<sub>2</sub>** and <sup>t</sup>BuCCH. However, with more acidic terminal alkynes such as MesCCH and PA, a different pathway is observed, involving an electronic and structural rearrangement accompanied by proton-shuttling, which may be self-promoted through a bimolecular mechanism. The charge state of the BDI ligand that is controlled by the degree of protonation plays a crucial role in directing the ordering of the frontier orbitals, which in turn modulates the reactivity of the vanadium complex. These features offer an intriguing mechanistic variation to the traditional metathesis pathway.<sup>20</sup> Evidence for such a process taking place is supported by the reaction of MesCCH with **1-OEt<sub>2</sub>** to yield a dMCBD scaffold in **5-Mes**. The formation of vanadabenzene ate complex, **6**, and the fact that its protonated derivative **6-H<sup>+</sup>** is active in PA polymerization supports the involvement of a cyclization mechanism in generating the cyclic polymeric morphologies. In future work, these initial experimental observations and computational results will be refined and tested further to optimize the catalytic activity. This study opens up exciting avenues for the controlled synthesis of novel cyclic polymers and highlights the potential of early transition metal catalysts in this field.

## ASSOCIATED CONTENT

**Supporting Information.** Supporting information is available free of charge on the ACS publication website, <http://pubs.acs.org>, at DOI: XXX and it includes: Supporting Information (PDF)  
Crystallographic information for **4-<sup>t</sup>Bu**: CCDC 2249030  
Crystallographic information for **5-Mes**: CCDC 2249031  
Crystallographic information for **6**: CCDC 2249032

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All authors have given approval to the final version of the manuscript.

### Funding Sources

We thank the US National Science Foundation (CHE-0848248, CHE-1152123, and CHE-2108266) and the University of Pennsylvania for the financial support of this research. The authors also acknowledge the NIH supplements award 3R01GM118510-03S1 and 3R01GM087605-06S1 and financial support of the Vagelos Institute for Energy Sciences and Technology for the purchase of NMR instrument NEO600. The computational part of this research was financially supported by the Institute for Basic Science in Korea (IBS-R10-A1).

## Notes

Any additional relevant notes should be placed here.

## ACKNOWLEDGMENT

We dedicate this work to the late Professor Robert Grubbs.

## ABBREVIATIONS

PA: Phenylacetylene;  
c-PPA: cyclic poly(phenylacetylene);  
l-PPA: linear poly(phenylacetylene);  
BDI<sup>-</sup>: β-diketimate ligand, [ArNC(CH<sub>3</sub>)<sub>2</sub>CH- (Ar = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>);  
dBDI<sup>2-</sup>: deprotonated β-diketimate,  
[ArNC(CH<sub>3</sub>)CHC(CH<sub>2</sub>)NAr]<sup>2-</sup> (Ar = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>);  
MGBD: metallacyclobutadiene;  
dMGBD: deprotonated metallacyclobutadiene;  
Mes: Mesityl;  
<sup>t</sup>Bu: *t*-butyl;  
sc-XRD: single-crystal X-ray Diffraction;  
PCM: Polarizable Continuum Model;  
SEC: Size-Exclusion Chromatography.

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