A Catalytically Relevant Intermediate in the Synthesis of Cyclic Polymers from Alkynes.

Journal:	*ChemComm*
Manuscript ID	CC-COM-07-2019-005612.R1
Article Type:	Communication

Chemical Communications

COMMUNICATION

A Catalytically Relevant Intermediate in the Synthesis of Cyclic Polymers from Alkynes.

Christopher D. Roland, Tianyu Zhang, Sudarsan VenkatRamani, Ion Ghiviriga, and Adam S. Veige*

2Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

A tungsten metallacyclopentadiene complex is generated upon treating a trianionic pincer tungsten alkylidyne with dipropargyl fluorene. The metallacyclopentadiene initiates the polymerization of alkynes to give cyclic polyacetylenes via ring expansion polymerization (REP).

An important challenge in modern polymer chemistry is the efficient and controlled synthesis of polymers with unique topologies.[1, 2] Perhaps the simplest shape change is to convert a linear polymer into its cyclic analogue. By simply tying together the chain ends of a linear polymer it is possible to dramatically alter its physical properties.[3] The repeat unit, functional groups, molecular weight (minus end groups), and polydispersity all remain the same when the chain ends are removed to create a cyclic polymer; however, the density,[4] refractive index,[5, 6] T_g,[7] viscoelasticity,[8] reptation,[9] crystallization[10] and surface properties[11, 12] all change.

A common method for the synthesis of cyclic polymers involves intramolecular coupling of polymer chain ends;[13, 14] however, inherent limitations of this method are the requirement of dilute conditions and long reaction times.[15] Ring closing[16, 17] and other methods[18-20] continue to improve[21] and provide at least an opportunity to obtain samples of unique ring-shaped polymers. A focus of this communication is *metal-catalysed* cyclic polymer synthesis. Exciting new transition metal based catalysts are emerging, and an important contribution includes ring expansion metathesis polymerization (REMP).[22-27] Critical to the REMP catalyst design is the presence of a cyclometalated alkylidene/carbene that ensures the polymer chain ends remain attached to the metal ion.[26-29] Application of REMP permits the synthesis of cyclic dendronized polymers[30] and cyclic brush polymers from norbornene based monomers.[31-36] It is now even possible to produce stereoregular cyclic polymers. We introduced two tungsten catalysts that produce syndiotactic and *cis*-enriched (>95%) cyclic polynorbornene.[37]

Another catalyst we discovered employs ring expansion polymerization (REP), but in a traditional insertion type mechanism.[38-40] Initially, an alkylidyne was proposed as the initiator,[39] but the realization that complexes **1** and **2** participate in the polymerization led us to propose an alternative mechanism that culminates in the production a cyclic polymer.[38]

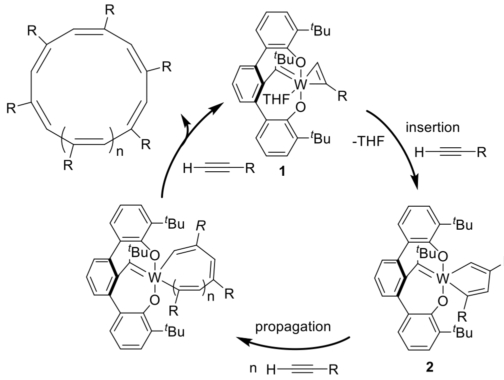

Figure 1. Proposed mechanism for the catalytic synthesis of cyclic polyacetylenes.

In trial polymerizations using compound **1** and monitored by ^{1}H NMR spectroscopy, it was apparent that a significant portion of the initiator remained in the dormant state even after consumption of all monomer. Unreacted initiator is symptomatic of slow initiation/rapid propagation kinetics. Thus, the initial insertion of alkyne into the metallacyclopropene to form **2** must be slow, but subsequent insertions into the metallacyclopentadiene must be extremely rapid, giving rise to high catalyst activities.[40] This report centres on attempts to improve initiation rates by directly synthesizing a catalytically relevant metallacyclopentadiene similar to **2**.

---

[a] *University of Florida, Department of Chemistry, Center for Catalysis, P.O. Box 117200, Gainesville, FL, 32611.*

Electronic Supplementary Information (ESI) available: [Synthesis protocols, NMR, polymer characterization]. See DOI: 10.1039/x0xx00000x

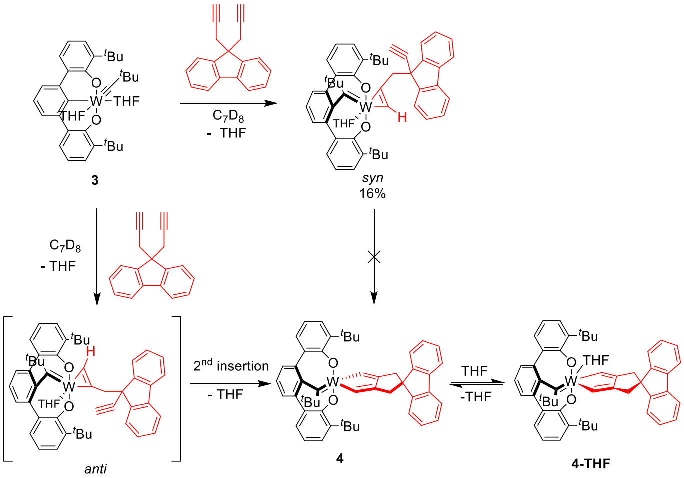

Figure 2. Preparation of metallacyclopentadiene **4** and subsequent equilibration between **4**/**4-THF**.

To trap the metallacyclopentadiene intermediate, intermolecular alkyne insertion (propagation) must be prevented. Maximizing the chance of intramolecular insertion, dipropargylfluorene was chosen as the substrate. Treating an orange solution of the parent alkylidyne complex **3** with dipropargylfluorene in benzene at ambient temperature produces a dark purple solution within 5 min. As designed, the proximity of the geminal dialkynes promotes intramolecular insertion to form the trigonal bipyramidal metallacyclopentadiene complex **4**. Presumably, coordination of one alkyne occurs first followed by insertion of the second pendant alkyne. Evidence for this mechanism comes from a minor impurity (16%) that is tentatively assigned as the singly bound alkyne complex, where due to a *syn* (alkyne substituent relative to alkyldene) orientation the second alkyne cannot insert. Due to its low concentration however, complete characterization was not possible though some chemical shifts recorded in toluene-*d$_8$* at 0 °C, are provided (see ESI). Initial alkyne binding with an *anti*-configuration presumably leads to the metallacyclopentadiene **4**.

Released upon forming the metallacyclopentadiene the THF can then re-enter the coordination sphere of complex **4** over 5.5 h to give the solvento complex **4-THF**. Evidence for the bound THF comes from a slight upfield shift and broadening of the THF protons in the ^{1}H NMR spectrum of **4-THF**.[41] Complexes **4** and **4-THF** are solution stable but decompose upon removal of solvent *in vacuo*. Cooling a concentrated ether solution of **4/4-THF** produces thin purple crystals that melt above -30 °C. Sublimation of a frozen benzene solution of the **4/4-THF** mixture yields a fine purple powder.

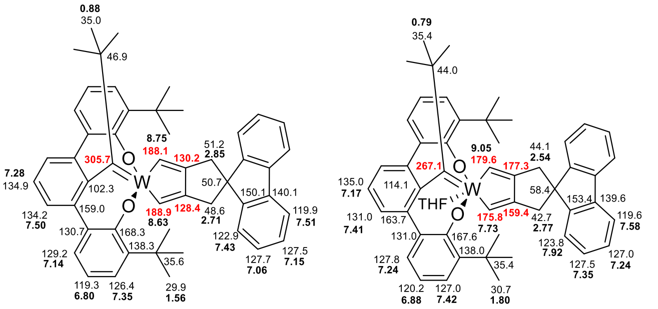

Figure 3. ^{1}H and ^{13}C chemical shifts assignments for **4** (left) and **4-THF** (right).

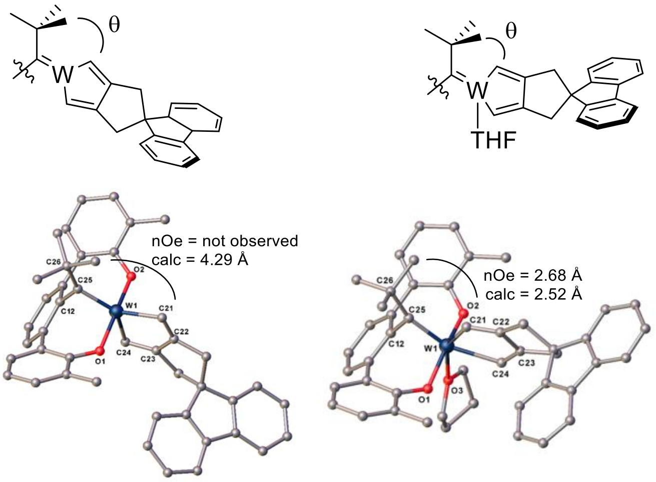

Figure 4. Computed model compounds for **4'** (left) and **4-THF'** (right); calculated versus nOe distances.

Confirmation of the identity of the initial complex **4** is possible by NMR spectroscopic techniques. The spectra of **4** and **4-THF** are similar, and the ^{1}H-^{13}C long-range couplings indicate the atom connectivities are identical, except of course for the proposed additional W-THF bond. Figure 3 provides the ^{1}H and ^{13}C chemical shifts for the two complexes. Both complexes exhibit pseudo C_s symmetry with the mirror plane containing the tetrahydropentalene, the metallacyclopentadiene and the *t*-butylalkylidene moieties, thus rendering the two *o*-^{t}Bu groups, flanking pincer aromatic rings, and the two sets of geminal methylene protons in the tetrahydropentalene equivalent. The most notable differences between **4** and **4-THF** are the resonances attributable to the carbon atoms within the metallacyclopentadiene. For example, in complex **4** the α-carbons resonate at 188.9 and 188.1 ppm, while the β-carbons resonate at 128.4 and 130.2 ppm. In contrast, the same positions in complex **4-THF** appear at 179.6 and 175.8 ppm for the α-carbons, and the β-carbons appear at 177.3 and 159.4 ppm. Evident from the 47.1 and 31.0 ppm downfield shifts, the β-carbons in **4-THF** clearly experience a much different electronic environment. Another significant shift occurs for the alkylidene carbon. In complex **4**, the alkylidene carbon appears at 305.7 ppm, and in complex **4-THF** the alkylidene carbon shifts upfield to 267.1 ppm. Two previously published (one structurally characterized) analogous W-metallacyclopentadienes, *without* a bound THF exhibit alkylidene carbon resonances at 310.0 and 309.9 ppm, giving credence to the assignment of **4**.[40] For **4-THF**, the dramatic upfield shift to 267.1 ppm for the alkylidene carbon fits with previously published six-coordinate *THF-bound* OCO^{4-} alkylidenes that range between 251.7 and 268.8 ppm.[40]

More support for the structural assignment comes from calculated model complexes depicted in Figure 4. The model complex bond lengths and angles for **4'** agree well with the X-ray structure of an analogous complex (see ESI Table S8). Highlighted in the calculated structures are the distances between the ^{t}Bu protons on the alkylidene and α-proton on the metallacyclopentadiene. In complex **4'** the calculated distance is 4.29 Å, whereas in **4-THF'** the distance is significantly shorter (2.52 Å) due to the need to accommodate the coordinated THF molecule. nOe data provides strong support for this change in ligand orientation upon THF coordination. Selective inversion of the metallacyclopentadiene proton at 8.75 ppm within **4** *does not* exhibit a nOe with the ^{t}Bu protons on the alkylidene. However, selective inversion of the equivalent proton on **4-THF** at 9.05 ppm provides a nOe corresponding to an average distance of 2.68 Å, very similar to the calculated value of 2.52 Å. Several other nOe calculated distances are consistent with the structural assignments (see ESI Tables S2 and S4). Single point calculated molecular orbitals of the computed structures provide insight into the dramatic change in ^{13}C NMR chemical shifts of the β-carbons upon coordinating THF and lend further support for their assignments. The HOMO of **4'** comprises mostly W=C π-bond character, whereas the HOMO of **4-THF'** delocalizes over the W=C π-bond *and* the metallacyclopentadiene, thus explaining the >30 ppm shift upon coordinating THF.

Following the ^{1}H NMR resonances of the CH_2 protons during conversion of **4** to **4-THF** allows the kinetics to be measured (Figure 5). The methylene protons on complex **4** resonate as doublets at 2.71 and 2.85 ppm, whereas in **4-THF** they appear at 2.54 and 2.77 ppm. Integration of the methylene resonances and plotting ln[**4**]/[**4**]$_0$ vs time provides $k_{obs} = 1.41(\pm 0.04) \times 10^{-4}\ s^{-1}$ for the conversion of **4** to **4-THF**. Importantly, k_{obs} is the same ($1.64(\pm 0.15) \times 10^{-4}\ s^{-1}$) in the presence of 10-fold excess of THF. The zero-order in THF implies complex **4** must first undergo ligand reorganization prior to THF coordination (see ESI for full kinetics analysis).

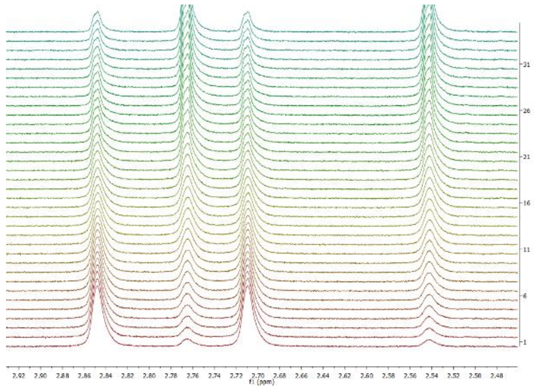

Figure 5. ^{1}H NMR spectra monitoring the conversion of **4** to **4**/**4-THF** in C_7D_8 at 25 °C.

Unable to isolate **4** or **4-THF**, polymerizations were conducted by generating **4** *in situ*. Combining complex **3** with dipropargylfluorene and stirring for 5 min generates **4** and injection of this initiator solution into toluene containing 5000 equiv of phenylacetylene initiates the production of cyclic polyphenylacetylene. Figure 6 depicts the root mean squared radius of gyration ($<R_g^2>^{1/2}$) vs molecular weight for an authentic sample of linear polyphenylacetylene, cyclic polyphenylacetylene generated by known cyclic polymer initiator **1**, and cyclic polyphenylacetylene generated by **4**. It is clear from the data that polymers produced by initiator **1** and **4** have smaller R_g values for the same molecular weight as a consequence of their cyclic topology, as compared to the linear polymer produced by Rh(COD)Cl.[42, 43]

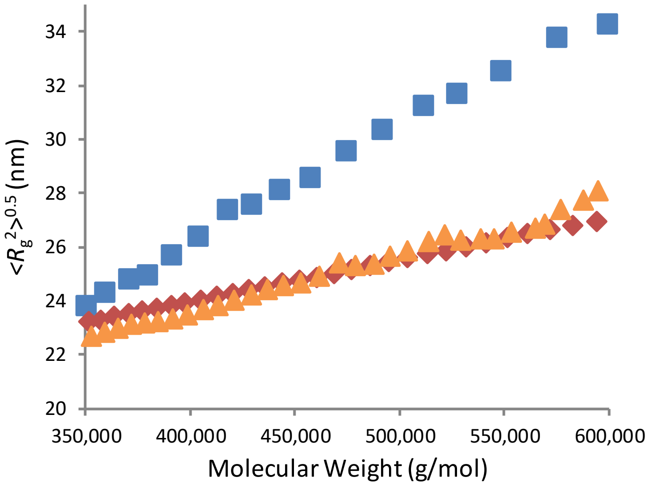

Figure 6. Comparison of $<R_g^2>^{1/2}$ versus molecular weight between linear polyphenylacetylene produced with initiator Rh(COD)Cl (BLUE) and cyclic polyphenylacetylenes produced by previously published initiator **1** (RED) and complex **4** generated *in situ* (orange). The smaller rms radii of the polymers produced by **1** and **4** supports the assignment of a cyclic topology.

Initiator **4** has a lower activity compared to the original initiator **1**. Under identical conditions the initial activity of **1** is $3.02 \times 10^6\ g_{pol}/mol_{cat}/h$ (after 5 min), whereas, **4** exhibits an activity of $2.12 \times 10^6\ g_{pol}/mol_{cat}/h$. The differences in apparent initial rates are likely due to the presence of the bound alkyne in **1** versus the metallocyclopentadiene in **4**. After 25 min the overall conversions are 66% and 38% for **1** and **4**, respectively. Dispersities (Đ) for the two initiators are essentially the same at 1.9 after 25 min. The mixture of **4**/**4-THF** is also active for phenylacetylene polymerization.

In conclusion, the important discovery in this work is the identification of the viable catalytically active species **4**. The proposed mechanism for cyclic polymer synthesis via REP invokes a metallacyclopentadiene intermediate (Figure 1). Designed to rapidly insert two alkyne units, the dipropargyl alkyne monomer successfully generates the metallacyclopentadiene complex **4** and its comparable (albeit lower) polymerization activity confirms it is an intermediate in the synthesis of cyclic polymers. With two strongly donating aryloxides and an alkylidene, the tetraanionic pincer ligand is important in creating a coordination environment capable of multiple alkyne insertions. Rather than eliminating triphenyl benzene after three insertions, the strongly reducing environment of the pincer ligand may prevent reductive elimination, thus allowing the ring expansion and multiple alkyne insertions. Another important finding is the ability of complex **4** to undergo a ligand reorganization to allow THF to coordinate. The ability to rotate towards the alkylidene moiety to permit THF binding may be related to the high activity towards alkyne insertion and propagation. Now identified as a viable intermediate, another design feature that comes from this work is the metallacyclopentadiene fragment. It is plausible that other coordinatively unsaturated complexes containing metallacyclopentadienes in high oxidation states that are reluctant to undergo reductive elimination could produce cyclic polymers from alkynes.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This material is based upon work supported by the National Science Foundation CHE-1565654.

References

1. Y. Tezuka, *Topological Polymer Chemistry : Progress of Cyclic Polymers in Syntheses, Properties and Functions*, World Scientific Publishing Company, Singapore, SGP, 2012.
2. Y. Tomikawa, T. Yamamoto and Y. Tezuka, *Macromolecules*, 2016, **49**, 4076-4087.
3. T. Yamamoto and Y. Tezuka, *Soft Matter*, 2015, **11**, 7458-7468.
4. J. M. Garcia Bernal, M. M. Tirado, J. J. Freire and J. Garcia de la Torre, *Macromolecules*, 1991, **24**, 593-598.
5. D. J. Orrah, J. A. Semlyen and S. B. Ross-Murphy, *Polymer*, 1988, **29**, 1455-1458.
6. D. J. Bannister and J. A. Semlyen, *Polymer*, 1981, **22**, 377-381.
7. S. J. Clarson, K. Dodgson and J. A. Semlyen, *Polymer*, 1985, **26**, 930-934.
8. P. C. Griffiths, P. Stilbs, G. E. Yu and C. Booth, *J. Phys. Chem.*, 1995, **99**, 16752-16756.
9. P. G. Santangelo, C. M. Roland, T. Chang, D. Cho and J. Roovers, *Macromolecules*, 2001, **34**, 9002-9005.
10. H. Q. Zhang, T. X. Lv, J. Q. Li, B. Y. Liu and S. C. Jiang, *Cryst. Growth Des.*, 2019, **19**, 49-54.
11. A. Patel, T. Cosgrove and J. A. Semlyen, *Polymer*, 1991, **32**, 1313-1317.
12. Y. Jeong, Y. Jin, T. Chang, F. Uhlik and J. Roovers, *Macromolecules*, 2017, **50**, 7770-7776.
13. B. A. Laurent and S. M. Grayson, *J. Am. Chem. Soc.*, 2006, **128**, 4238-4239.
14. D. M. Eugene and S. M. Grayson, *Macromolecules*, 2008, **41**, 5082-5084.
15. B. A. Laurent and S. M. Grayson, *Chem. Soc. Rev.*, 2009, **38**, 2202-2213.
16. T. Josse, J. De Winter, P. Gerbaux and O. Coulembier, *Angew. Chem. Int. Ed.*, 2016, **55**, 13944-13958.
17. T. Yamamoto, S. Yagyu and Y. Tezuka, *J. Am. Chem. Soc.*, 2016, **138**, 3904-3911.
18. H. Sugita, M. Nojima, Y. Ohta and T. Yokozawa, *Polymer Chemistry*, 2019, **10**, 1182-1185.
19. P. Sun, J. Q. Chen, J. A. Liu and K. Zhang, *Macromolecules*, 2017, **50**, 1463-1472.
20. R. Okabayashi, Y. Ohta and T. Yokozawa, *Macromolecules*, 2017, **50**, 9589-9597.
21. J.-Q. Chen, L. Xiang, X. Liu, X. Liu and K. Zhang, *Macromolecules*, 2017, **50**, 5790-5797.
22. H. A. Brown and R. M. Waymouth, *Acc. Chem. Res.*, 2013, **46**, 2585-2596.
23. H. A. Brown, Y. A. Chang and R. M. Waymouth, *J. Am. Chem. Soc.*, 2013, **135**, 18738-18741.
24. E. J. Shin, W. Jeong, H. A. Brown, B. J. Koo, J. L. Hedrick and R. M. Waymouth, *Macromolecules*, 2011, **44**, 2773-2779.
25. I. Asenjo-Sanz, A. Veloso, J. I. Miranda, J. A. Pomposo and F. Barroso-Bujans, *Polym. Chem.*, 2014, **5**, 6905-6908.
26. C. W. Bielawski, D. Benitez and R. H. Grubbs, *Science*, 2002, **297**, 2041-2044.
27. C. W. Bielawski, D. Benitez and R. H. Grubbs, *J. Am. Chem. Soc.*, 2003, **125**, 8424-8425.
28. J. T. Ciszewski, B. H. Xie, C. S. Cao and A. L. Odom, *Dalton Trans.*, 2003, DOI: 10.1039/b311320p, 4226-4227.
29. K. S. Lokare, R. J. Staples and A. L. Odom, *Organometallics*, 2008, **27**, 5130-5138.
30. A. J. Boydston, T. W. Holcombe, D. A. Unruh, J. M. J. Frechet and R. H. Grubbs, *J. Am. Chem. Soc.*, 2009, **131**, 5388-5389.
31. Y. Xia, A. J. Boydston and R. H. Grubbs, *Angew. Chem. Int. Ed.*, 2011, **50**, 5882-5885.
32. K. Zhang, M. A. Lackey, Y. Wu and G. N. Tew, *J. Am. Chem. Soc.*, 2011, **133**, 6906-6909.
33. K. Zhang, Y. P. Zha, B. Peng, Y. M. Chen and G. N. Tew, *J. Am. Chem. Soc.*, 2013, **135**, 15994-15997.
34. K. Zhang and G. N. Tew, *ACS Macro Lett.*, 2012, **1**, 574-579.
35. K. Zhang and G. N. Tew, *React. Funct. Polym.*, 2014, **80**, 40-47.
36. A. J. Boydston, Y. Xia, J. A. Kornfield, I. A. Gorodetskaya and R. H. Grubbs, *J. Am. Chem. Soc.*, 2008, **130**, 12775-12782.
37. S. S. Nadif, T. Kubo, S. A. Gonsales, S. VenkatRamani, I. Ghiviriga, B. S. Sumerlin and A. S. Veige, *J. Am. Chem. Soc.*, 2016, **138**, 6408-6411.
38. C. D. Roland, H. Li, K. A. Abboud, K. B. Wagener and A. S. Veige, *Nat. Chem.*, 2016, **8**, 791-796.
39. S. Sarkar, K. P. McGowan, S. Kuppuswamy, I. Ghiviriga, K. A. Abboud and A. S. Veige, *J. Am. Chem. Soc.*, 2012, **134**, 4509-4512.
40. K. P. McGowan, M. E. O'Reilly, I. Ghiviriga, K. A. Abboud and A. S. Veige, *Chem. Sci.*, 2013, **4**, 1145-1155.
41. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.
42. P. Mastrorilli, C. F. Nobile, A. Rizzuti, G. P. Suranna, D. Acierno and E. Amendola, *J. Mol. Catal. A: Chem*, 2002, **178**, 35-42.
43. O. Trhlíková, J. Zedník, H. Balcar, J. Brus and J. Sedláček, *J. Mol. Catal. A: Chem*, 2013, **378**, 57-66.