

and washed with hexane. Thus obtained was *fac*-[Mo(phen)(CO)₃PN(Me)CH₂CH₂NMe(OMe)] (8) (1.07 g, 2.10 mmol, 81%). Anal. Calcd for C₂₀H₂₁MoN₄O₄P: C, 47.26; H, 4.16; N, 11.02. Found: C, 47.13; H, 4.22; N, 10.84.

[Mo(phen)(CO)₃PN(Me)CH₂CH₂NMe]⁺ (9). The synthesis is identical with that of 5 except that it was carried out by using 8 (162 mg, 0.32 mmol).

fac-[Mo(bpy)(CO)₃P(NEt₂)(OMe)₂] (10). A solution of [Mo(bpy)(CO)₄] (325 mg, 0.89 mmol) and P(NEt₂)(OMe)₂ (0.34 mL, 323 mg, 1.99 mmol) in toluene (15 mL) was refluxed for several hours. After the solution was cooled to room temperature, hexane was added to give a precipitate, which was recrystallized from CH₂Cl₂/hexane. Thus obtained was *fac*-[Mo(bpy)(CO)₃P(NEt₂)(OMe)₂] (10) (308 mg, 0.61 mmol, 69%). Anal. Calcd for C₁₉H₂₄MoN₃O₅P: C, 45.52; H, 4.83; N, 8.38. Found: C, 45.56; H, 5.08; N, 8.09.

fac-[Mo(bpy)(CO)₃P(NEt₂)₂(OMe)] (11). A solution of [Mo(bpy)(CO)₄] (500 mg, 1.37 mmol) and P(NEt₂)₂(OMe) (0.7 mL, 3.05 mmol) in xylene (20 mL) was refluxed for about 1 h. After the solution was cooled to room temperature, hexane was added to give a precipitate, which was recrystallized from CH₂Cl₂/hexane. Thus obtained was *fac*-[Mo(bpy)(CO)₃P(NEt₂)₂(OMe)] (11) (467 mg, 0.88 mmol, 64%). Anal. Calcd for C₂₂H₃₁MoN₄O₄P: C, 48.71; H, 5.76; N, 10.33. Found: C, 48.45; H, 6.02; N, 10.11.

Reaction of 5 with NaOEt. To a CH₂Cl₂ solution containing 5 (0.57 mmol) was added NaOEt (80 mg, 1.18 mmol) at -78 °C.

The solution was allowed to warm to room temperature and stirred for 2 h. After removal of NaOEt which remained unreacted by filtration, the filtrate was loaded on a silica gel column. The violet portion eluted with CH₂Cl₂ was collected, and the solvent was removed. The resulting powder was recrystallized by CH₂Cl₂/hexane. Thus obtained was *fac*-[Mo(bpy)(CO)₃PN(Me)CH₂CH₂NMe(OEt)] (7) (228 mg, 0.46 mmol, 80%).

Reaction of 5 with LiMe. To a CH₂Cl₂ solution containing 5 (0.61 mmol) was added a LiMe ether solution (0.61 mmol) at -78 °C. After being allowed to warm to room temperature, the solution was concentrated and loaded on a silica gel column. The violet portion eluted with CH₂Cl₂ was collected, and hexane was added to give a powder. Thus obtained was *fac*-[Mo(bpy)(CO)₃PN(Me)CH₂CH₂NMe(Me)] (12) (173 mg, 0.37 mmol, 60%). Anal. Calcd for C₁₈H₂₁MoN₄O₃P: C, 46.16; H, 4.53; N, 11.97. Found: C, 45.92; H, 4.61; N, 11.82.

Reaction of 5 with HNEt₂. To a CH₂Cl₂ solution containing 5 (0.90 mmol) prepared from 6 and BF₃·OEt₂ was added HNEt₂ (0.3 mL, 0.36 g, 4.92 mmol) at -78 °C, and then the solution was allowed to warm to room temperature. The product was purified by column chromatography as in the case of 12. Thus obtained was 6 (339 mg, 0.70 mmol, 78%).

Acknowledgment. We thank Mr. Akira Mizumo and Mr. Yoshihisa Toda in Material Science & Analysis Laboratories, Mitsui Petrochemical Industry, LTD, for ³¹P NMR and ¹³C NMR measurements.

Living Polymerization of 2-Butyne Using a Well-Characterized Tantalum Catalyst

Kevin C. Wallace, Andy H. Liu, William M. Davis, and Richard R. Schrock*

Department of Chemistry, Room 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Ta(CHCMe₃)(DIPP)₃(THF) (DIPP = 2,6-diisopropylphenoxide) reacts with 1 equiv of 2-butyne, diphenylacetylene, bis(trimethylsilyl)acetylene, or 2-methyl-1-buten-3-yne to give THF-free metallacyclobutene complexes 1, 2, 3a, and 4a, respectively. Addition of pyridine to 3a and 4a yields simple monoadducts 3b and 4b while addition of pyridine to 1 and 2 yields vinylalkylidene complexes 5 and 6 by opening of the metallacyclobutene ring. Ta[C(Me)C(Me)CHCMe₃](DIPP)₃(py) (5) crystallizes in the monoclinic system, space group *P*2₁/*n*, with *a* = 14.791 (4) Å, *b* = 19.716 (4) Å, *c* = 16.115 (5) Å, *V* = 4668 (4) Å³, β = 96.60 (3)°, *Z* = 4, *fw* = 916.07, and ρ = 1.30 g/cm³. The distorted trigonal-bipyramidal molecule contains an equatorial vinylalkylidene ligand (Ta=C = 1.99 (2) Å) in which the *tert*-butyl group is *cis* to the methyl group on the C=C linkage. 5 reacts with up to 200 equiv of 2-butyne readily to give living polymers Ta[C(Me)C(Me)]₂CHCMe₃(DIPP)₃(py) from which the organic polymer can be cleaved by treatment with benzaldehyde and shown to have a very low polydispersity (<1.05). If only 1 equiv of 2-butyne is added to 5, then a side product, Ta[C(Me)C(Me)C[C(Me)(CH₂CMe₃)]CH₂(DIPP)₃ (8), a tantalacyclopentene complex, forms virtually quantitatively. 8 crystallizes in the monoclinic system, space group *P*2₁/*c*, with *a* = 10.632 (4) Å, *b* = 12.750 (9) Å, *c* = 34.144 (9) Å, *V* = 4627 (6) Å³, β = 91.42 (3)°, *Z* = 4, *fw* = 891.06, and ρ = 1.279 g/cm³. 8 does not form in the presence of excess 2-butyne. Block copolymers containing 2-butyne and norbornene can be prepared. Analogous reactions between 2-butyne and Ta(CHCMe₃)(TIPT)₃(THF) (TIPT = 2,4,6-triisopropylbenzenethiolate) were not successful.

Introduction

Polymers made from acetylenes have received much attention in recent years. The interest in polyacetylene itself can be ascribed to the fact that it is a good conductor when doped,¹ while polymers made from substituted acetylenes have properties that make them desirable as selective membranes for gases and liquids.^{2,3} The two most common mechanisms for polymerization of acetylenes

by transition-metal catalysts are thought to be insertion of an acetylene into a metal-carbon single bond (eq 1)⁴⁻⁷ and addition of an acetylene to a metal-carbon double bond to give a metallacyclobutene complex which opens to give a complex with a new metal-carbon double bond (eq 2).^{2,8-11} (Other mechanisms have been proposed.^{12,13}) Evidence for the "insertion" mechanism (eq 1) has been

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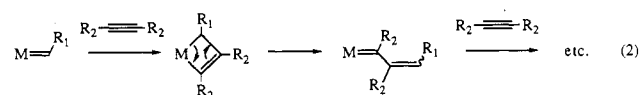
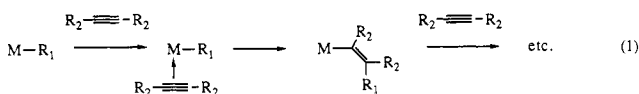
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accumulating for many years, but evidence for the "metathesis" mechanism (eq 2) is still relatively scarce.



The metathesis mechanism was first proposed by Masuda and co-workers¹⁴ in order to explain the polymerization of phenylacetylene by WCl_6 and MoCl_5 . Several observations support this mechanism for some catalysts containing a group V or VI metal. For example, a tantalum alkylidene complex is known to react with diphenylacetylene to give a new vinylalkylidene complex.¹⁵ Similar reactions for Fischer-type carbene complexes have been proposed,¹⁶ and acetylenes are polymerized by such species under a variety of conditions.^{8,11,16} Acetylenes also are polymerized by Fischer-type carbyne complexes¹⁷ as well as classical olefin metathesis catalysts.⁹ Nutation NMR experiments¹⁰ have been proposed as a means of determining whether the insertion or the metathesis mechanism is operative.

Tantalum alkylidene complexes of the general formula $\text{Ta}(\text{CHCMe}_3)_3\text{X}_3(\text{B})$ ($\text{X} = 2,6$ -diisopropylphenoxide (DIPP), 2,4,6-triisopropylbenzenethiolate (TIPT); $\text{B} = \text{THF}$, pyridine)¹⁸ will polymerize norbornene in a controlled manner (cf. titanocene catalysts, the first catalysts for "living ROMP"¹⁹). The mechanisms for the two tantalum catalyst systems differ significantly, however. Tantalacyclobutane complexes are the lowest energy species in the DIPP system while alkylidenes are the lowest energy species in the TIPT catalyst system. We now find that the DIPP complexes will react with some substituted acetylenes in a controlled manner. In one case the resulting complex is a catalyst for the living polymerization of 2-butyne. Again we find that differences between the DIPP and TIPT systems are substantial but, more surprisingly, that the balance of factors within the DIPP system itself that leads to a successful living polymerization is extremely delicate.

Results

Formation of Metallacyclobutene Complexes and Their Reactions with Bases. $\text{Ta}(\text{CHCMe}_3)_3(\text{DIPP})_3$ (THF) reacts with 1 equiv of 2-butyne, diphenylacetylene,

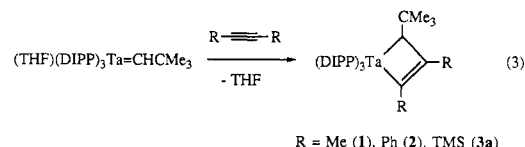
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Table I. NMR Data for the MC_2 Ring in Metallacyclobutene Complexes^a

| compound | H_α | C_α (J_{CH}) | C_β (J_{CH}) |
|--|-------------------|---------------------------------------|--------------------------------------|
| $\text{Ta}[\text{C}(\text{Me})\text{C}(\text{Me})\text{CH}(\text{CMe}_3)]_3$ - (DIPP) ₃ (1) | 2.71 (s) | 84.1 (d, 134) 217.9 (s) | 156.2 (s) |
| $\text{Ta}[\text{C}(\text{Ph})\text{C}(\text{Ph})\text{CH}(\text{CMe}_3)]_3$ - (DIPP) ₃ (2) | 3.32 (s) | 87.7 (d, 132) 224.0 (s) | 151.6 (s) |
| $\text{Ta}[\text{C}(\text{SiMe}_3)\text{C}(\text{SiMe}_3)\text{CH}(\text{CMe}_3)]_3$ (DIPP) ₃ (3a) | 3.99 (s) | 59.9 (d, 116) 254.8 (s) | 232.2 (s) |
| $\text{Ta}[\text{C}(\text{SiMe}_3)\text{C}(\text{SiMe}_3)\text{CH}(\text{CMe}_3)]_3$ (DIPP) ₃ (py) (3b) | 3.99 (s) | | |
| $\text{Ta}[\text{CH}_2\text{C}(\text{Me})\text{C}(\text{CHCHCMe}_3)]_3$ (DIPP) ₃ (4a) | 2.15 (s) | 57.3 (t, 141) 216.9 (s) | 150.5 (s) |
| $\text{Ta}[\text{CH}_2\text{C}(\text{Me})\text{C}(\text{CHCHCMe}_3)]_3$ (DIPP) ₃ (py) (4b) | 1.76 (s) | 56.7 (t, 140) 212.8 (s) | 148.2 (s) |

^a Listed in ppm vs TMS; solvent = C_6D_6 and temperature = 25 °C unless otherwise noted.

and bis(trimethylsilyl)acetylene to give THF-free metallacyclobutene complexes 1 (quantitatively), 2 (79%), and 3a (43%), respectively (eq 3). ¹H and ¹³C NMR data are

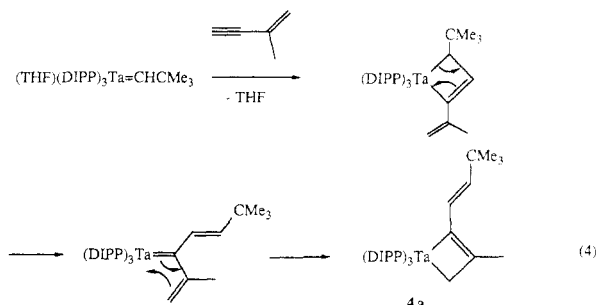


listed in Table I. An alternative possible formulation, vinylalkylidene complexes formed by rearrangement of the tantalacyclobutene ring, can be ruled out on the basis of the H_α chemical shifts (3–4 ppm) and CH_α coupling constants (aliphatic) and by the fact that two of the metallacycles have been converted into authentic vinylalkylidene complexes by addition of pyridine (see later). The chemical shift for the α -carbon atom that does not have a proton bound to it alone is insufficient evidence for the metallacyclobutene structure, since the α -carbon resonance is found in the region 215–255 ppm and therefore could be ascribed to an alkylidene α -carbon atom. Resonances for only one type of DIPP ligand are observed in the room-temperature spectra for all tantalacycle complexes, indicating that the phenoxide ligands exchange rapidly. (Similar behavior was observed for phenoxide complexes of unsymmetrically substituted tantalacyclobutanes.¹⁹) The geometric configuration of the ligands around tantalum in these complexes is not known; in related tantalacyclobutane structures the geometry ranged from trigonal bipyramidal to distorted square pyramidal.¹⁹ The formation of stable metallacyclobutene complexes in these reactions contrasts with the result of the reaction between $\text{TaCp}(\text{CHCMe}_3)\text{Cl}_2$ and diphenylacetylene, where the presumed intermediate metallacyclobutene complex opened to yield the vinylalkylidene complex.¹⁵ Other examples of metallacyclobutene complexes are known, e.g., those formed by adding acetylenes to " $\text{TiCp}_2(\text{CH}_2)$ ".²⁰

$\text{Ta}(\text{CHMe}_3)_3(\text{DIPP})_3(\text{THF})$ also reacts with 2-methyl-1-buten-3-yne to give a metallacyclobutene complex (4a), but not the one expected from a simple addition reaction. The ¹H and ¹³C NMR data (Table I) are consistent with a metallacyclobutene complex containing an α -methylene group in the ring and a side chain containing two inequivalent olefinic protons. We propose the reaction sequence shown in eq 4. Rearrangement of the initially

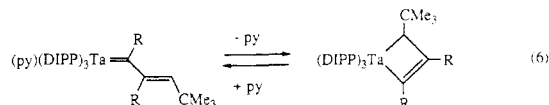
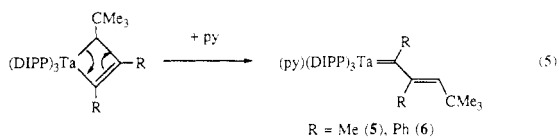
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formed metallacyclobutene complex that contains an α -*tert*-butyl group to **4a** can be ascribed to a relief of steric congestion.



The metallacyclobutene complexes **1**, **2**, **3a**, and **4a** do not react with more of the acetylene they were made from, the exception being a reaction between 2-butyne and **1** to give a small amount of intractable polymer. (This behavior will be discussed later.) Likewise, when Ta(CHCMe₃)-(DIPP)₃(THF) is treated with an excess of any of the acetylenes mentioned, only metallacyclobutene complexes are observed, and again only in the case of 2-butyne is some intractable polymer formed.

Complexes **1**, **2**, **3a**, and **4a** were treated with pyridine in the hope that the metallacyclobutene rings would open to give vinylalkylidene complexes and that the vinylalkylidene complexes might react further with acetylenes in a controlled manner. Addition of pyridine to **3a** and **4a** only give base adducts, yellow **3b** and orange **4b** (see Table I and Experimental Section). However, complexes **1** and **2** react with pyridine to give the purple vinylalkylidene complexes **5** and **6**, respectively (eq 5). The



C_{α} chemical shifts for these alkylidene complexes (Table II) are similar to those observed for TaCp[C(Ph)C(Ph)CHCMe₃]Cl₂,¹⁵ the α -carbon resonance in **6** was found at 243.1 ppm, but two downfield resonances were observed for **5** (at -60°C) at 256.4 and 232.1 ppm (see later). Full NMR characterization of these complexes is complicated by the fact that they are in equilibrium with the corresponding metallacyclobutene complexes (eq 6) in solution at ambient and elevated temperatures. For example the room-temperature ¹H and ¹³C NMR spectra of **5** display no distinct resonances for any of the three equilibrating carbon atoms, C _{α} , C _{β} , and C _{γ} (see Experimental Section for details), and at elevated temperatures only resonances for **1** are observed in addition to those for free pyridine.

The structure of **5** was confirmed by an X-ray study. A drawing is shown in Figure 1a, a view of the core is shown in Figure 1b, and relevant bond distances and angles are given in Table III. The geometry of **5** is about halfway between a trigonal bipyramid and a square pyramid.²¹ The angle between the two DIPP ligands (containing O(1)

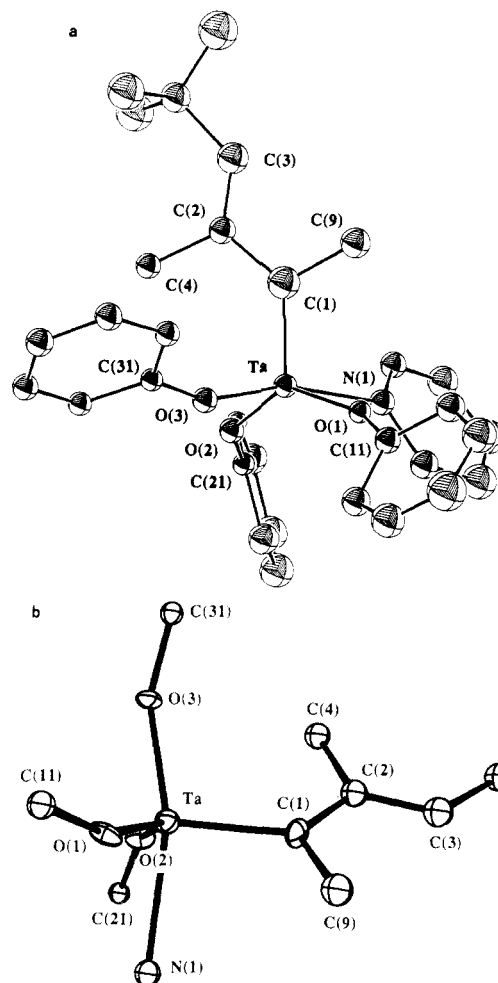


Figure 1. (a) An ORTEP drawing of Ta[C(Me)C(Me)CHCMe₃](DIPP)₃(py) (**5**) (35% ellipsoids; isopropyl groups and hydrogen atoms omitted for clarity). (b) A view of the core of **5**.

Table II. NMR Data for the Alkylidene Ligand in Tantalum Vinylalkylidene Complexes^a

| compound | CHCMe ₃ | C _{α} |
|--|--------------------|----------------------------------|
| Ta[C(Me)C(Me)CHCMe ₃](DIPP) ₃ (py) (5) ^b | 6.57 (s) | 256.4 |
| | c | 232.1 |
| Ta[C(Me)C(Me)] _n CHCMe ₃ (DIPP) ₃ (py) (7) | 5.2–5.4 (br) | 258.3 |
| Ta[C(Ph)C(Ph)CHCMe ₃](DIPP) ₃ (py) (6) | d | 243.1 |
| Ta[C(Ph)C(Ph)CHCMe ₃]CpCl ₂ ¹⁵ | e | 259 |

^a Listed in ppm versus TMS; solvent = C₆D₆ and temperature = 25 $^{\circ}\text{C}$ unless otherwise noted. ^b In toluene-*d*₈ at -60°C . ^c Another resonance is thought to occur in the complex region between 6.7 and 7.2 ppm. ^d Obscured in region between 6.7 and 7.5 ppm. ^e Obscured in region between 6.3 and 7.3 ppm.

and O(2)) is 139.8 (5) $^{\circ}$, while the angles between C(1) and the DIPP ligands that contain O(2) and O(1) are 105.5 (7) $^{\circ}$ and 111.1 (6) $^{\circ}$, respectively. As shown in Figure 1b, O(1) and O(2) are displaced slightly toward the axial pyridine ligand (N(1)–Ta–O(1) = 80.3 (5) $^{\circ}$, N(1)–Ta–O(2) = 82.4 (6) $^{\circ}$, and C(1)–Ta–N(1) = 91.7 (8) $^{\circ}$), away from the axial DIPP ligand (O(2)–Ta–O(3) = 91.5 (5) $^{\circ}$, O(1)–Ta–O(3) = 96.2 (5) $^{\circ}$, and C(1)–Ta–O(3) = 102.9 (8) $^{\circ}$). The Ta–O bond lengths in **5** (average = 1.92 (2) Å) are similar to those observed in other tantalum DIPP complexes.^{18,22} In a

(21) (a) A reviewer pointed out that the description of the structure can be quantitated if one makes the reasonable assumption that the geometry lies on the Berry pseudorotation coordinate connecting a trigonal bipyramid with a square pyramid.^{21b} Using the dihedral angle method he calculates the geometry of **5** to be 58% of the way from a TBP toward a square pyramid. We thank the reviewer for his time and interest. (b) Holmes, Robert R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

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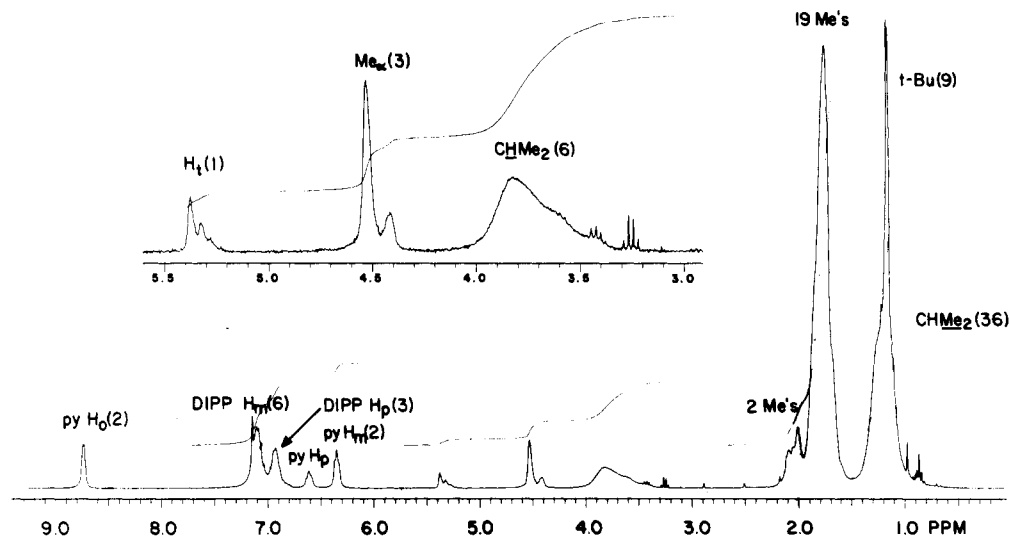


Figure 2. The ^1H NMR spectrum of **5** after reaction with 10 equiv of 2-butyne in C_6D_6 .

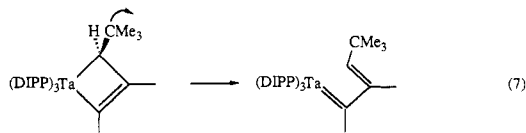
Table III. Selected Bond Distances (Å) and Angles (deg) in $\text{Ta}[\text{C}(\text{Me})\text{C}(\text{Me})\text{CHCMe}_3](\text{DIPP})_3(\text{py})$ (**5**)

| | | | |
|--------------|-----------|---------------|-----------|
| Ta-C(1) | 1.90 (3) | C(1)-Ta-O(1) | 111.1 (7) |
| Ta-O(1) | 1.93 (1) | C(1)-Ta-O(2) | 105.5 (6) |
| Ta-O(2) | 1.94 (1) | C(1)-Ta-O(3) | 102.9 (8) |
| Ta-O(3) | 1.88 (1) | N(1)-Ta-O(1) | 80.3 (5) |
| Ta-N(1) | 2.28 (2) | N(1)-Ta-O(2) | 82.4 (6) |
| C(1)-C(2) | 1.53 (3) | N(1)-Ta-O(3) | 165.2 (5) |
| C(2)-C(3) | 1.36 (3) | C(1)-Ta-N(1) | 91.7 (8) |
| O(1)-Ta-O(2) | 139.8 (5) | Ta-O(1)-C(11) | 157 (1) |
| O(2)-Ta-O(3) | 91.5 (5) | Ta-O(2)-C(21) | 141 (1) |
| O(1)-Ta-O(3) | 96.2 (5) | Ta-O(3)-C(31) | 157 (1) |

trigonal bipyramid the alkylidene carbon atom C(1) would occupy an equatorial position; in a square pyramid it would occupy an axial position. An important point is that no matter which description of this species is chosen, the pyridine ligand is in a position *cis* to C(1), a position where an acetylene also is likely to bind. This structure is similar overall to that of a related dinitrogen complex, $(\text{THF})_2(\text{DIPP})_3\text{Ta}=\text{NN}=\text{Ta}(\text{DIPP})_3(\text{THF})$,^{22a} in which a distorted trigonal-bipyramidal geometry was observed with the N_2^{4-} ligand occupying an equatorial site and THF occupying an axial site.

The Ta-C(1) bond distance of 1.90 (3) Å is consistent with a tantalum-carbon double bond.²³ Bond lengths in the alkylidene ligand are consistent with the vinyl-substituted alkylidene proposal; e.g., C(1) and C(2) are separated by 1.53 (3) Å, and C(2) and C(3) are separated by 1.36 (3) Å. A dihedral angle between the planes defined by Ta-C(1)-C(9) and C(4)-C(2)-C(3) of $\sim 10^\circ$ reveals that the vinylalkylidene ligand is slightly twisted about the C(1)-C(2) bond. The alkylidene ligand also is twisted about the Ta-C(1) bond (Figure 1b).

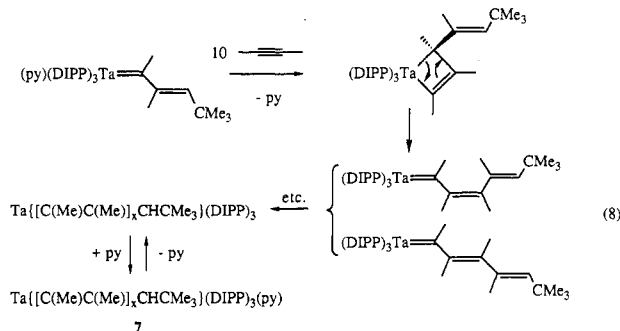
An important feature of **5** is the *cis* configuration of the *tert*-butyl and methyl group about the double bond. A *cis* configuration most likely originates because of steric crowding during ring opening (eq 7).



Let us return to the NMR spectrum of **5**. At -60°C an ^1H NMR spectrum of **5** in toluene- d_8 displays resonances for two types of pyridine ligands (broad $\text{py H}_{\text{ortho}}$ resonances at 8.64 and 8.22 ppm, $\sim 1:3$ ratio). Two resonances

also were seen for other substituents such as the methyl group on the α -carbon atom of the alkylidene ligand at 4.34 and 4.18 ppm. A low-temperature ^{13}C NMR spectrum (-60°C , toluene- d_8) revealed two alkylidene carbon signals at 246.4 (major) and 232.0 ppm (minor). We cannot exclude the possibility that the two types of complexes present at low temperatures are the two in which the *tert*-butyl group is *cis* or *trans* to the β -methyl group, even though the *trans* configuration is observed in the solid state, since the cyclobutene ring could re-form and open again to reach a different equilibrium of *cis* and *trans* isomers in solution. However, we think it most likely that we are observing isomers (at -60°C) that differ slightly in the relative orientations of the ligands in these crowded molecules as a result of restricted rotation of the bulky ligands or even a mixture of closely related, but distinct geometric isomers (e.g., square pyramidal and trigonal bipyramidal). Note that at elevated temperatures **5** loses pyridine and **1** reforms; near room temperature the interconversion of **5** and **1** probably is the major process being observed in the ^1H NMR spectrum.

Polymerization of 2-Butyne by $\text{Ta}[\text{C}(\text{Me})\text{C}(\text{Me})\text{CHCMe}_3](\text{DIPP})_3(\text{py})$. When **5** was treated with 10 equiv of 2-butyne in C_6D_6 , the solution changed from dark purple to deep red. An ^1H NMR spectrum showed that all 2-butyne and **5** had been consumed and a mixture of oligomers of 2-butyne¹⁷ capped by tantalum (**7**, eq 8; Figure



2; Table II) had formed. No resonances for a tetrasubstituted metallacyclobutene complex, a necessary intermediate in this reaction, were observed. Broad resonances (at least two) between 5.2 and 5.4 ppm that have a total area equal to one proton can be assigned to the terminal proton in the chain. We assign the two broad overlapping singlets at ~ 4.55 and ~ 4.45 ppm ($\sim 4:1$ ratio, Figure 2) of total area three to the methyl group on the α -carbon atom of the alkylidene ligand of **7** (average $x = 11$). The

(23) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum Press: New York, 1986.

broad resonances at ~ 2 ppm (area ~ 6) probably can be ascribed to the methyl groups on the β - and δ -carbon atoms of the chain, while the major broad resonance at ~ 1.8 ppm (~ 19 methyl groups) can be ascribed to the remaining methyl groups in the chain. (The resonance for the methyl groups in poly(2-butyne) has been reported to be at ~ 1.6 ppm in CDCl_3 .¹⁷) There are at least two resonances for the *tert*-butyl group, and all ligand resonances are broad.

When the solvent was removed in vacuo from the sample prepared by treating **5** with 10 equiv of 2-butyne and the resulting solid redissolved in C_6D_6 , an ^1H NMR spectrum indicated that less than 1 equiv of pyridine was present, and the pyridine resonances were broad. Therefore pyridine appears to bind only relatively weakly to the metal in **7**. We propose that the increased steric demand of the growing polymer makes loss of pyridine from **7** easier than loss of pyridine from **5**. Note that a *tetrasubstituted* metallacyclobutene complex is *not* formed when pyridine is lost from the metal, most likely for steric reasons. Loss of pyridine and failure to form a tantalacyclobutene ring both play an important role in establishing the circumstances for rapid chain growth.

It is clear that some fluxional process or a combination of processes (loss of pyridine, a change in geometry about the metal, or some concerted motion of interlocking ligands) broadens the pyridine and DIPP ligand resonances in the ^1H NMR spectrum of **7** (Figure 2). However, the multiplicity of resonances (primarily two) for H_t , Me_a , and the *tert*-butyl groups must arise for some other reason. If we assume that the chains are long enough in $\text{Ta}[\{\text{C}(\text{Me})\text{C}(\text{Me})\}_x\text{CMe}_3\text{(DIPP)}_3(\text{py})$ (average $x = 11$) so that differences that arise from chains of different lengths only lead to some relatively slight broadening of a given resonance, then different resonances must result from some relatively local *cis* versus *trans* geometries about a double bond. For example, two *tert*-butyl resonances could result from a mixture of *cis* and *trans* geometries of the first or the second double bond but probably not the third double bond from the end of the chain. For reasons mentioned earlier we feel that the first double bond is most likely *trans* and that *cis* or *trans* double bonds can arise in the growing chain because of less discrimination in the ring-opening step when the substituent is the growing chain instead of the *tert*-butyl group. Similar arguments could be used to explain other multiple resonances, e.g., for Me_a .

Poly(2-butyne) can be prepared at room temperature quantitatively and rapidly by using **5** as a catalyst; 100 equiv can be polymerized within 30 min, and the organic polymers can be cleaved from the metal with benzaldehyde (eq 9). A tantalum oxo complex is the proposed metal- $\text{Ta}[\{\text{C}(\text{Me})\text{C}(\text{Me})\}_x\text{CHCMe}_3\text{(DIPP)}_3(\text{py}) + \text{PhCHO} \rightarrow \text{PhCH}[\{\text{C}(\text{Me})\text{C}(\text{Me})\}_x\text{CHCMe}_3 + \text{"Ta(O)(DIPP)}_3(\text{py})"$ (9)

containing product of the cleavage reaction on the basis of analogous reactions between $\text{Ta}(\text{CHCMe}_3)(\text{DIPP})_3(\text{THF})$ and benzaldehyde.¹⁸ $\text{"Ta(O)(DIPP)}_3(\text{py})"$ is only one of several plausible oxo complexes; no isolation was attempted. Poly(2-butyne) samples prepared from **5** are rubbery and show a limited solubility in common organic solvents. Samples are most soluble in benzene or toluene, somewhat less soluble in methylene chloride, and only sparingly soluble in pentane. (Limited solubilities for polymers of symmetrically substituted acetylenes have been documented.^{2,8,17}) For this reason we did not attempt to prepare polymers containing more than 200 equiv of 2-butyne. Although the *trans/cis* ratio in these polymers is not known, evidence presented above suggests that both *cis* and *trans* configurations about the double bond will

Table IV. The Results of GPC Analysis of Polyacetylenes^a

| run | cat. | 2-butyne | other | $M_n(\text{uncorr})$ | M_w/M_n |
|------------------|------|----------|-----------------|--------------------------------------|-------------|
| 1 | 5 | 50 | 0 | 3 900 | 1.04 |
| 2 | 5 | 100 | 0 | 7 400 | 1.03 |
| 3 | 5 | 150 | 0 | 11 200 | 1.03 |
| 4 | 5 | 100 | 0 | 9 900 ^b | 1.05 |
| 5 | 5 | 200 | 0 | 17 900 ^b | 1.03 |
| 6 ^{i,f} | 5 | 100 | 0 | 7 400 | 1.03 |
| 7 ^{i,f} | 5 | 100 | 0 | 7 300 | 1.03 |
| 8 ^{i,f} | 5 | 100 | 0 | 7 400 | 1.03 |
| 9 | 5 | 0 | 100 (1-pentyne) | 13 700 ^c | 1.21 |
| | 5 | 0 | 100 (1-pentyne) | 13 000 ^d | 1.30 |
| 10 | 5 | 0 | 200 (1-pentyne) | 15 900 | 2.60 |
| 11 ^f | 5 | 50 | 50 (NBE) | 15 100 ($\sim 75\%$) | 1.12 |
| | | | | 332 800 ($\sim 20\%$) | 1.39 |
| 12 ^f | 5 | 100 | 100 (NBE) | 46 200 ^b ($\sim 70\%$) | 1.07 |
| | | | | 400 000 ^b ($\sim 30\%$) | ~ 1.50 |
| 13 ^f | e | 50 | 50 (NBE) | 18 400 ($\sim 50\%$) | 1.23 |
| | | | | 219 500 ($\sim 50\%$) | 1.41 |
| 14 ^g | 8 | 100 | 0 | 16 900 ($\sim 80\%$) | 1.03 |
| | | | | 66 800 ($\sim 20\%$) | 1.20 |
| 15 | h | 100 | 0 | 6 900 | 1.47 |

^a GPC solvent = methylene chloride with UV/vis detection unless otherwise noted; RI detection used for runs 9 and 10. In all block copolymer experiments, polymerization of the first monomer was confirmed before the second monomer was added. ^b GPC solvent is toluene, and the detection method is refractive index. ^c 15-min sample. ^d 60 min sample. ^e Catalyst = $\text{Ta}[\text{CH}(\text{C}_5\text{H}_9)\text{CHCH}^t\text{Bu}](\text{DIPP})_3$; 2-butyne was added after polymerization of NBE and subsequent addition of 3 equiv of pyridine. ^f Some loss of catalyst after polymerization of the first monomer was evident by GPC (as discussed in the text). ^g In presence of 2 equiv of pyridine. ^h Catalyst = $\text{Ta}(\text{CHCMe}_3)(\text{TIPT})_3(\text{THF})$. ⁱ After polymerization of 50 equiv of 2-butyne the solvent was removed in vacuo and the sample redissolved in toluene and 0 (run 6), 1 (run 7), or 10 (run 8) equiv of pyridine were added. An additional 50 equiv of 2-butyne were then polymerized.

be present throughout the polymer chain.

Samples of poly(2-butyne) prepared in this manner are essentially monodisperse with molecular weights that increase in proportion to the number of equivalents employed (runs 1–5, Table IV; Figure 3). Low polydispersity and a stepwise increase in molecular weight are indicative of a living polymerization reaction by a single mechanism with a virtually quantitative initiation at a rate that is of the same magnitude or larger than the rate of propagation. The living polymer can be aged before quenching without significantly broadening the molecular weight distribution. Therefore secondary metathesis of the double bonds in the polymer chain is slow, most likely because all double bonds but the terminal one are *tetrasubstituted*. (In contrast secondary metathesis of disubstituted double bonds in polynorbornene after consumption of norbornene leads to an increase in polydispersity.¹⁸) To our knowledge this is the first time that essentially monodisperse poly(2-butyne) has been prepared. The only other reports of living polymerizations of acetylenes are those by Masuda and Higashimura and co-workers²⁴ where polydispersities between 1.07 and 1.23 were observed for 1-chlorooct-1-yne and (*o*-(trimethylsilyl)phenyl)ethyne.

Pyridine does not play a significant role in the living polymerization of 2-butyne by **5**. Fifty equivalents of 2-butyne were polymerized by **5** to give **7** ($x_{av} = 51$) in toluene. The solvent was then removed in vacuo and the catalyst redissolved in toluene and treated with 50 additional equiv of 2-butyne in the presence of 0, 1, and 10 equiv of pyridine; the rates of poly(2-butyne) formation were qualitatively indistinguishable, and the resulting

(24) (a) Masuda, T.; Yoshimura, T.; Fujimori, J.; Higashimura, T. *J. Chem. Soc., Chem. Commun.* 1987, 1805. (b) Yoshimura, T.; Masuda, T.; Higashimura, T. *Macromolecules* 1988, 21, 1899.

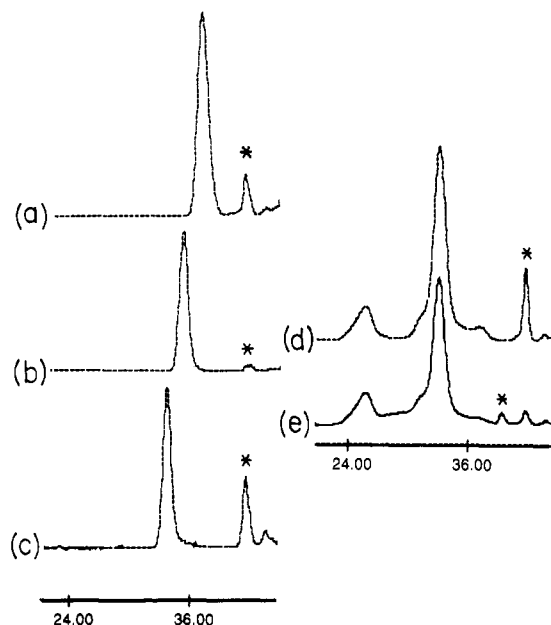


Figure 3. GPC traces for the benzylidene-capped poly(2-butyne) formed by reaction of **5** with (a) 50 equiv, (b) 100 equiv, and (c) 150 equiv, of 2-butyne, and GPC traces for a benzylidene capped block copolymer formed by reaction of **5** with 50 equiv of 2-butyne and 50 equiv of norbornene ((d) UV/vis detection; (e) refractive index detection): x axis, minutes; *, highest molecular weight solvent peak.

polymers virtually identical (runs 6, 7, 8). In these reactions an estimated 5–10% of the product consisted of poly(2-butyne) containing 50 equiv of monomer (in addition to that containing 100 equiv of monomer). When 50 equiv of 2-butyne were polymerized followed by 50 more equiv of 2-butyne *without* removing the solvent between additions, none of the polymer containing 50 equiv of monomer was observed. Therefore we suspect that a small amount of the first (50 equiv) living polymer was hydrolyzed by traces of water during manipulation.

Complex **6** does not react readily with diphenylacetylene. NMR studies show that it does react with 10 equiv of 2-butyne to give poly(2-butyne), but initiation must be significantly slower than propagation since little **6** is consumed during the polymerization process. The alkylidene in **6** should be significantly less reactive than that in **5** for steric reasons and possibly also because of the phenyl ring should deactivate the alkylidene α -carbon atom as a nucleophile.

Reaction of Ta[C(Me)C(Me)CHCMe₃](DIPP)₃(py) with 1 Equiv of 2-Butyne. Addition of 1 equiv of 2-butyne to Ta[C(Me)C(Me)CHCMe₃](DIPP)₃(py) (**5**) in ether gave a red solution from which a deep red oil was obtained after removing the solvent in vacuo. A deep red precipitate could be isolated readily from pentane at -30 °C, and upon standing more dilute pentane solutions at -30 °C for several days, light orange crystals could be obtained. ¹H NMR spectra of the red precipitate and the orange crystals were identical. They showed a single product (**8**) having a characteristic set of five singlets at 2.91 (area 2), 2.51 (2), 2.19 (3), 2.12 (3), and 1.74 (3) ppm in addition to resonances for the DIPP ligands and a *tert*-butyl group but no resonances for pyridine (Figure 4). No resonances were observed in the region for olefinic protons. Spectra at elevated temperatures were identical with those at 25 °C. A ¹³C NMR spectrum of the red precipitate displayed the expected resonances for the DIPP ligands and the *tert*-butyl group, along with resonances at 214.0 (s), 158.7 (s), 148.9 (s), 129.2 (s), 82.3 (t, $J_{\text{CH}} = 119$

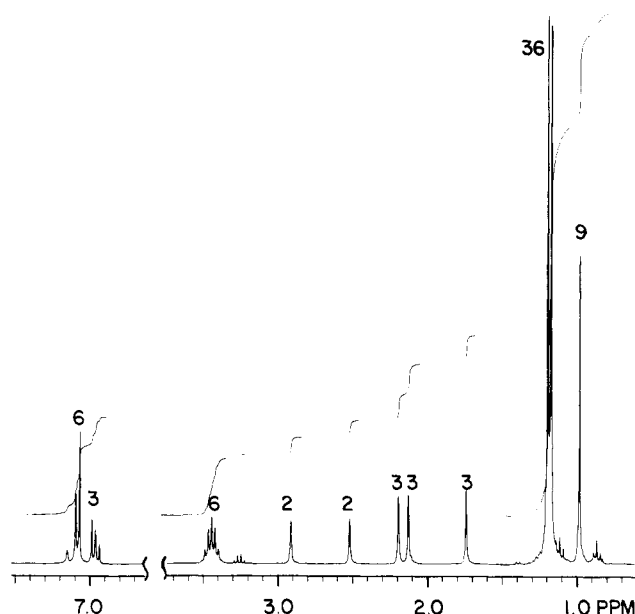


Figure 4. The ¹H NMR spectrum of Ta[C(Me)C(Me)C[C(Me)(CH₂CMe₃)]CH₂(DIPP)₃ (**8**) in C₆D₆.

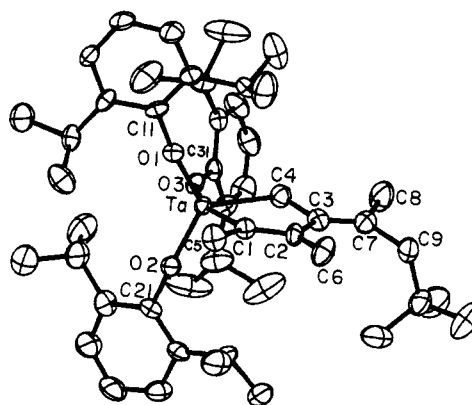


Figure 5. A view of Ta[C(Me)C(Me)C[C(Me)(CH₂CMe₃)]CH₂(DIPP)₃ (**8**).

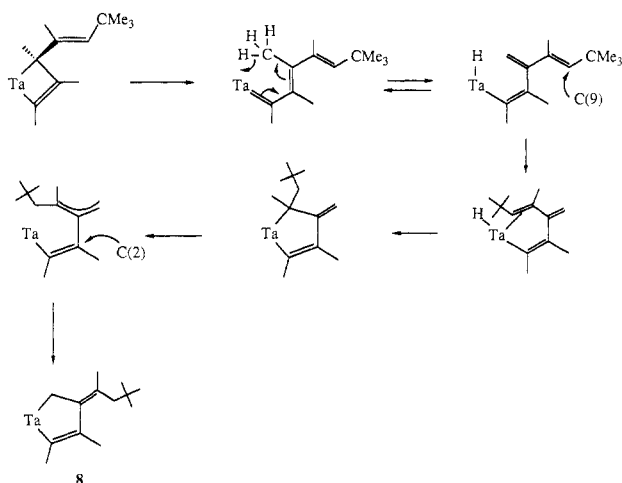
Table V. Selected Bond Distances (Å) and Angles (deg) in Ta[C(Me)C(Me)C[C(Me)(CH₂CMe₃)]CH₂(DIPP)₃ (**8**)

| | | | |
|--------------|-----------|----------------|-----------|
| Ta-O(1) | 1.857 (7) | O(1)-Ta-C(4) | 115.9 (3) |
| Ta-O(2) | 1.860 (7) | O(2)-Ta-C(1) | 93.9 (3) |
| Ta-O(3) | 1.917 (7) | O(2)-Ta-C(4) | 122.1 (4) |
| Ta-C(1) | 2.12 (1) | O(3)-Ta-C(1) | 154.1 (3) |
| Ta-C(4) | 2.18 (1) | O(3)-Ta-C(4) | 80.8 (4) |
| C(1)-C(2) | 1.35 (1) | C(1)-Ta-C(4) | 73.3 (4) |
| C(2)-C(3) | 1.46 (1) | C(11)-O(1)-Ta | 171.7 (6) |
| C(3)-C(7) | 1.35 (1) | C(21)-O(2)-Ta | 158.6 (7) |
| C(3)-C(4) | 1.52 (1) | C(31)-O(3)-Ta | 151.8 (6) |
| O(1)-Ta-O(2) | 121.4 (3) | C(2)-C(1)-Ta | 122.8 (8) |
| O(1)-Ta-O(3) | 98.9 (3) | C(3)-C(4)-Ta | 116.7 (7) |
| O(2)-Ta-O(3) | 97.8 (3) | C(1)-C(2)-C(3) | 115 (1) |
| O(1)-Ta-C(1) | 94.4 (3) | C(2)-C(3)-C(4) | 110 (1) |

Hz), and 47.5 (t, $J_{\text{CH}} = 124$ Hz) ppm and three methyl resonances. A second equivalent of 2-butyne apparently has been incorporated into **5** to give "Ta(2-butyne)₂-(CHCMe₃)(DIPP)₃," but NMR data were inconsistent with formation of either a simple metallacyclobutene or alkylidene complex, the two most likely products.

An X-ray study revealed that **8** has the formula Ta[C(Me)C(Me)C[C(Me)(CH₂CMe₃)]CH₂(DIPP)₃ and contains a tantalacyclopentene ring. An ORTEP drawing of **8** is shown in Figure 5, and relevant bond distances and angles are given in Table V. The overall geometry of **8** is approximately halfway between a trigonal bipyramid and a

Scheme I. A Possible Mechanism of Forming 8



square pyramid. Bond distances and angles for the DIPP ligands are not unusual for d^0 complexes of this general nature (average Ta–O bond length = 1.878 (7) Å; average Ta–O–C = 160.7 (6)°, and the Ta–C bond distances are in the expected range for tantalum carbon single bonds (2.12 (1) Å and 2.18 (1) Å).²³ The metallacyclopentene ring is virtually planar with internal angles of 73.3 (4)° at Ta, 122.8 (8)° at C(1), 115 (1)° at C(2), 110 (1)° at C(3), and 116.7 (7)° at C(4). The double bonds C(1)–C(2) (1.35 (1) Å) and C(3)–C(7) (1.35 (1) Å) are clearly distinguishable from single bonds such as C(3)–C(4) (1.52 (1) Å).

A possible mechanism of formation of 8 is shown in Scheme I. The key step is reversible activation of a proton in a methyl group in a trienylidene complex to give a trienyl hydride complex. Coordination of the terminal (trisubstituted) double bond followed by transfer of the hydride to C(9) would yield the exo methylene tantalacyclopentene complex related to 8. In order to relieve steric strain this tantalacycle rearranges to 8 via a π allylic intermediate. Note that the neopentyl group in the allyl must be located syn with respect to C(2) in order to end up in the observed position in the final product. This is the expected result since syn-substituted allyl ligands are generally more stable than anti-substituted allyl ligands.²⁵ (It is worth pointing out that other exotic but selective rearrangements of tantalacyclic ring systems have been documented.²⁶) An important point is that 8 arises only when ~ 1 equiv of additional 2-butyne is added. When excess 2-butyne is present, then chain growth competes with the reaction shown in Scheme I, and only a trace of 8 is observed (Figure 2). After a third equivalent of 2-butyne has been incorporated, then only tetrasubstituted double bonds will be accessible to the tantalum hydride ligand. Therefore we propose that this type of termination reaction *cannot occur after 3 equiv of 2-butyne have been incorporated into the chain*, although reversible CH activation in the methyl group could still occur throughout polymer growth. Since the living polymer is stable to any rearrangement reaction after all 2-butyne has been consumed, CH activation is not simply kinetically blocked by a more rapid reaction of the Ta=C bond with more 2-butyne.

Complex 8 does not react in a controlled fashion with additional 2-butyne; only starting material and a small

amount of intractable polymer are observed at room temperature. (The intractable polymer is thought to be produced by a small amount of some highly active catalyst, perhaps formed by hydrolysis of 8 by traces of water.) However, 8 will react with 2-butyne in the presence of pyridine to give a soluble polymer. GPC analysis of a polymer prepared employing 100 equiv of 2-butyne (Table IV) showed it to be essentially monodisperse, but with a higher than expected molecular weight ($M_n = 16900$, $d = 1.03$). A small but significant amount ($\sim 20\%$) of a higher molecular weight polymer ($M_n = 66800$, $d = 1.20$) also was present. When 15–20 equiv of pyridine are added to a sample of 8 in C_6D_6 , the only noticeable difference in the spectrum is that all resonances are slightly broadened. When a sample of 8 containing 1 equiv of pyridine was heated to 65 °C, a very broad resonance for a new species centered around 3.7 ppm was noted in addition to the resonances for 8. The new species accounts for $\sim 10\%$ of the sample at 65 °C. Upon cooling the sample back to room temperature, however, only resonances for 8 are observed. The species formed at high temperature in the presence of pyridine has not been identified, but it appears to be similar to 7, if not identical, on the basis of the chemical shift of its DIPP methyne resonances. Formation of 7 ($x = 2$) at room temperature in the presence of pyridine followed by rapid polymer growth therefore *could* be the mechanism of polymerization of some of the 2-butyne by 8 in the presence of pyridine, but formation of some higher molecular weight polymer suggests that there is more than one mechanism for forming polymer from 8 in the presence of pyridine, at least under the conditions we have employed so far. Related problems arise upon attempting to prepare block copolymers containing 2-butyne (see below).

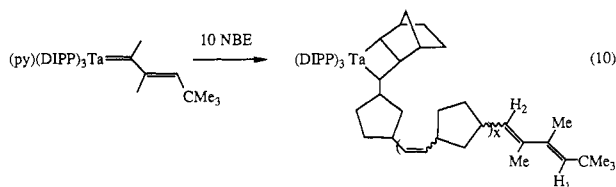
Attempts To Polymerize 1-Pentyne. Addition of 100 equiv of 1-pentyne to 5 in toluene gives a deep orange solution; the solution remains deep orange upon addition of benzaldehyde. Removal of the solvent in vacuo yields an oily orange polymer with $M_n = 13700$ and $d = 1.21$ (run 9, Table IV). When the same reaction is performed with 200 equiv of 1-pentyne (run 10), the resulting polymer has a low M_n and a relatively high polydispersity, a circumstance that could be the result of significant deactivation of the catalyst during the polymerization process. Deactivation could result from reactions similar to the one proposed above for formation of 8. Additionally, or alternatively, certain di- and trisubstituted metallacyclobutenes may form in the reaction involving 1-pentyne that are stable to ring opening and further reaction with 1-pentyne. Other deactivation reactions are also plausible, e.g., metathesis of the growing polymer chain leading to a polymer with a higher dispersity and possibly cyclic organic products. In fact, the dispersity of poly(1-pentyne) formed from reaction of 5 with 1-pentyne does increase with reaction time (Table IV), consistent with secondary metathesis reactions, now involving di- or trisubstituted double bonds in the polymer chain, depending on regiochemistry. In any case, living polymerization of 1-pentyne (and we assume other terminal acetylenes) with 5 is not nearly as successful as that of 2-butyne, and the mechanism of polymerization is not understood.

Preparation of Poly(2-butyne)/Polynorbornene Block Copolymers. Essentially monodisperse polynorbornene has been prepared employing the tantalacyclobutane complex $Ta[CH(C_5H_9)CHCHCMe_3](DIPP)_3$ as a catalyst in a reaction whose rate is determined by the rate at which the TaC_3 ring opens to give the incipient alkylidene complex.¹⁸ Therefore we felt it may be possible to

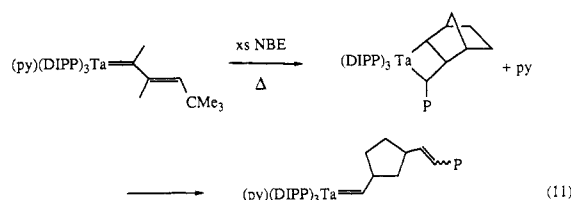
(25) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

(26) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* 1980, 102, 5610.

prepare 2-butyne/norbornene block copolymers. Norbornene (10 equiv) was added to **5** in C_6D_6 at room temperature, and the solution was heated at 50 °C until all NBE was consumed. The 1H NMR spectrum showed resonances characteristic of a propagating tantalacyclobutane species analogous to those seen for $Ta[CH(C_5H_9)CHCHCMe_3](DIPP)_3$.¹⁸ Furthermore, resonances for H_1 (s, ~ 5.7 ppm) and H_2 (d, ~ 5.1 ppm; see eq 10)



could be observed. When **5** was treated with 100 equiv of NBE and the solution heated to 50 °C until all NBE was consumed (see Experimental Section for details), the cleaved polymer had a value of $M_n = 18700$ and a polydispersity of 1.04. A trace amount of a higher molecular weight polymer also was observed; we propose as a result of a competing “base-on” polymerization mechanism analogous to that proposed earlier.¹⁸ The difference is that in this case the polydispersity of the polynorbornene did not increase after all NBE had been consumed, as was the case employing $Ta[CH(C_5H_9)CHCHCMe_3](DIPP)_3$, a fact that suggests that pyridine inhibits secondary metathesis. Toward the end of the polymerization reaction of NBE by **5**, the color of the solution changed from colorless to light yellow (not observed for NBE polymerization by $Ta[CH(C_5H_9)CHCHCMe_3](DIPP)_3$), consistent with formation of an alkylidene species (eq 11). We have confirmed that



when 100 equiv of NBE are polymerized by $Ta[CH(C_5H_9)CHCHCMe_3](DIPP)_3$ at 65 °C in the presence of 3 equiv of pyridine, the nearly colorless reaction turns yellow after ~ 45 min and the polydispersity of the resulting polynorbornene increases to only 1.14 after 1 h and 1.25 after 3 h, instead of the increase to 1.6–1.9 in the absence of added pyridine.^{18b}

Related reactions involving the sequential polymerization of 2-butyne and norbornene by **5** do result in the formation of block copolymers, according to GPC and 1H NMR studies, although there are complications. The polymerization of 50 equiv of 2-butyne by **5** was first confirmed by quenching and examining an aliquot by GPC, and then 50 equiv of NBE was added and the solution was heated until all NBE had been consumed. The polymer was cleaved off with benzaldehyde in the usual way. A polymer was formed whose approximate molecular weight (versus polystyrene) was consistent with that of the expected block copolymer ($M_n = 15100$, $d = 1.12$; $\sim 75\%$; Table IV). But a higher molecular weight polymer ($M_n = 332800$, $d = 1.39$; $\sim 20\%$; Figure 3) also was formed, along with a small amount of poly(2-butyne) ($M_n = 4200$, $d = 1.04$; 6%). The poly(2-butyne) probably arises from hydrolysis losses. Similar results were obtained employing 100 equiv each of 2-butyne and norbornene (Table IV). A plausible explanation for the formation of both the expected block copolymer and a higher molecular weight polymer (also thought to be a block copolymer) is com-

petition between the relatively well-behaved “base-free” polymerization mechanism and a still poorly defined “base-on” mechanism, respectively, for polymerizing norbornene.¹⁸ It should be noted that the “base-on” mechanism for forming polynorbornene starting with **5** apparently does *not* compete successfully under the conditions employed (see above), possibly because pyridine is labilized in the initial metallacycle formed from **5** (even though it is apparently less labile in **5** itself; see above). Interaction of the trisubstituted double bond in the side chain of the initial metallacycle with the metal may labilize pyridine at this stage.

Other attempts to prepare monodisperse block copolymers, e.g., employing $Ta[CH(C_5H_9)CHCHCMe_3](DIPP)_3$ as the catalyst (run 13) also led to the formation of both the expected polymer and a high molecular weight polymer (Table IV).

Polymerization of Acetylenes with $Ta(CHCMe_3)(TIPT)_3(THF)$. The ability of $Ta(CHCMe_3)(TIPT)_3(THF)$ ($TIPT = 2,4,6-SC_6H_2-i-Pr_3$) to polymerize acetylenes also was explored briefly since it is an effective catalyst for polymerizing norbornene, albeit by a different mechanism than that of the analogous DIPP complex.¹⁸ We now know (unpublished results) that the structure of $Ta(CHCMe_3)(TIPT)_3(THF)$ is significantly different from that of the analogous DIPP complex and so might expect its mechanism of reacting with norbornene to be different for that reason alone.

Polymerization of 100 equiv of 2-butyne by $Ta(CHCMe_3)(TIPT)_3(THF)$ yielded a relatively poorly defined polymer ($M_n = 6900$) with a relatively large polydispersity (1.47; Table IV) and a low molecular weight tail. Secondary metathesis can be ruled out since thiolate alkylidene complexes do not react even with ordinary olefins¹⁸ and therefore certainly will not react with terasubstituted double bonds. We cannot offer an explanation for this behavior at this stage.

Attempts to isolate intermediates in reactions between $Ta(CHCMe_3)(TIPT)_3(THF)$ and acetylenes failed. Thiolate complexes tend to be much more soluble than analogous phenoxide complexes, thereby making isolation of intermediates relatively difficult (in our experience so far) relative to the ease of isolating intermediate phenoxide complexes.

Discussion

The results reported here demonstrate the feasibility of controlled polymerization of an acetylene using a relatively easily prepared, well-defined transition-metal catalyst and lend considerable support to the metathesis mechanism for acetylene polymerization. Catalyst activity at 25 °C is high, and an added bonus is the potential for endcapping poly(2-butyne) with interesting functionalities using the Wittig-like capping reaction. These results extend the list of living polymerizations by well-characterized transition-metal complexes.^{18,19,27}

What was initially surprising is the specificity of this system for 2-butyne, at least under the conditions we have used so far. Complex **5** will not polymerize 3-hexyne, 1-phenyl-1-propyne, or 1-(trimethylsilyl)-1-propyne, and polymerization of 1-pentyne gives a relatively poorly defined polymer. For example, when **5** is treated with excess 3-hexyne, approximately 1 equiv of 3-hexyne appears to

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be incorporated (by ^1H NMR), but no further reaction is observed at room temperature or 65°C . Perhaps a deactivation reaction analogous to that shown in Scheme I is now competitive with a chain growth, since chain growth is likely to be slower for steric reasons. This predicament illustrates the extent to which versatility and generality must be sacrificed for control. With more traditional catalysts such as a metal halide combined with a main-group alkyl as a cocatalyst, a range of acetylenes can be polymerized but only recently has there been any report²⁴ that polymers having a relatively low polydispersity can be prepared (between 1.07 and 1.23 for 1-chloro-1-octyne and (*o*-(trimethylsilyl)phenyl)ethyne).

The results of attempts to prepare low polydispersity block copolymers of 2-butyne and norbornene illustrate the problem that arises when the mechanisms of polymerization of the two monomers differ. Norbornene is polymerized both by rate-limiting ring opening of a base-free tantalacyclobutane complex and also in competition by an as yet poorly defined "base-on" mechanism in which pyridine (in this case) remains bound to the metal.^{18b} A bimodal distribution results. These and other problems appear to arise in part from the fact that metallacycles are simply too stable toward ring opening to give alkylidenes. Therefore in the future it may prove more fruitful to employ well-characterized W^{28a} or Mo^{28b} alkylidene catalysts for acetylene polymerization, since in general metallacyclobutane complexes appear to be less stable for Mo or W than they are for Ta or Ti.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by using standard Schlenk techniques. Reagent grade ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. All deuterated NMR solvents were passed through a column of activated alumina.

$\text{Ta}(\text{CHCMe}_3)(\text{DIPP})_3(\text{THF})$, $\text{Ta}[\text{CH}(\text{C}_6\text{H}_5)\text{CHCMe}_3](\text{DIPP})_3$, and $\text{Ta}(\text{CHCMe}_3)(\text{TIPT})_3(\text{THF})$ were prepared as described in the literature.¹⁸ All other reagents were purchased from commercial sources and purified by standard techniques.

Chemical shifts are listed in parts per million downfield from TMS. Coupling constants are quoted in hertz. Routine multiplicities and coupling constants are not listed. The NMR solvent is benzene- d_6 and the temperature 25°C unless otherwise noted. All polymer samples were analyzed in toluene or methylene chloride (after passage through a $0.5\text{-}\mu\text{m}$ disposable filter unit; $\sim 0.3\%$ by weight polymer in solution) at 25°C versus polystyrene standards ($(1260\text{--}1.030) \times 10^6$ MW) on one of two GPC systems: (i) a Waters 150C instrument equipped with three Styragel columns (10^3 , 10^4 , and 10^5 Å), a refractive index detector, and a Waters Data Module for data analysis or (ii) a GPC system employing a Rheodyne Model 7125 sample injector, a Kratos Spectroflow 400 pump, five Shodex GPC columns (KF-802, 802.5, 803, 804, and 805), a Kratos Spectroflow 757 UV/VIS absorbance detector, a Knauer Model R981 refractive index detector, and a MacAdios Model 411 and Macintosh Plus computer for data analysis. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory (Woodside, NY) of Spang Microanalytical Laboratory (Eagle Harbor, MI).

Preparation of Compounds. $\text{Ta}[\text{C}(\text{Me})\text{C}(\text{Me})\text{CH}(\text{CMe}_3)](\text{DIPP})_3$ (**1**). A solution of 2-butyne (9.2 μL , 0.12 mmol) in ether (5 mL) was cooled to -30°C and added to a stirred solution of $\text{Ta}(\text{CHCMe}_3)(\text{DIPP})_3(\text{THF})$ (0.100 g, 0.12 mmol) in ether (5 mL) at -30°C . The solution turned orange. After 10

min the solution was filtered through Celite, and the solvent was removed in vacuo to give an orange oil. A ^1H NMR spectrum of this oil in C_6D_6 showed only the product. Orange crystals were isolated from pentane at -40°C . In an analogous experiment starting with 300 mg of $\text{Ta}(\text{CHCMe}_3)(\text{DIPP})_3(\text{THF})$ 200 mg of product was isolated (68%): ^1H NMR δ 7.07 (d, 6, H_m), 6.93 (t, 3, H_p), 3.61 (septet, 6, CHMe_2), 2.71 (br s, 1, H_α), 2.40 (d, 3, $\text{J}_{\text{HH}} = 2.6$, C_βMe), 2.06 (s, 3, C_αMe), 1.20 (d, 36, CHMe_2), 1.12 (s, 9, CMe_3); ^{13}C NMR δ 217.9 (s, C_α), 157.0 (s, C_{ipso}), 156.2 (s, C_β), 138.5 (s, C_α), 123.7 (d, C_m), 123.6 (d, C_p), 84.1 (d, $\text{J}_{\text{CH}} = 134$, C_α), 36.7 (CMe_3), 33.5 (CMe_3), 27.3 (CHMe_2), 24.3 (CHMe_2), 20.4 and 16.9 (Me's). Anal. Calcd for $\text{TaC}_{45}\text{H}_{67}\text{O}_3$: C, 64.56; H, 8.08. Found: C, 64.75; H, 8.12.

$\text{Ta}[\text{C}(\text{Ph})\text{C}(\text{Ph})\text{CH}(\text{CMe}_3)](\text{DIPP})_3$ (**2**). A solution of diphenylacetylene (0.063 g, 0.35 mmol) in ether (5 mL at -30°C) was added to a stirred solution of $\text{Ta}(\text{CHCMe}_3)(\text{DIPP})_3(\text{THF})$ (0.300 g, 0.35 mmol) in ether (10 mL at -30°C). The solution was warmed to room temperature and stirred for 60 min, during which time the color changed to orange. The solution was then filtered through Celite and the solvent removed from the filtrate in vacuo. The residue was recrystallized from pentane at -30°C to give an orange powder (0.266 g, 79%): ^1H NMR δ 7.48–6.76 (10, phenyl H resonances), 7.04 (6, H_m), 6.95 (3, H_p), 3.67 (6, CHMe_2), 3.32 (1, H_α), 1.14 (36, CHMe_2), 1.12 (unresolved, 9, CMe_3); ^{13}C NMR δ 224.0 (C_α), 157.0 (C_{ipso}), 151.6 (C_β), 143.6 (phenyl C_{ipso} 's), 138.6 (C_α), 130.1–125.9 (phenyl C's), 123.8 (C_m and C_p), 87.7 (d, $\text{J}_{\text{CH}} = 132$, C_α), 39.4 (CMe_3), 34.1 (CMe_3), 27.4 (CHMe_2), 24.5 (CHMe_2). Anal. Calcd for $\text{TaC}_{55}\text{H}_{71}\text{O}_3$: C, 68.72; H, 7.46. Found: C, 68.71; H, 7.44.

$\text{Ta}[\text{C}(\text{SiMe}_3)\text{C}(\text{SiMe}_3)\text{CH}(\text{CMe}_3)](\text{DIPP})_3$ (**3a**). A solution of bis(trimethylsilyl)acetylene (133 μL , 0.59 mmol) in ether (10 mL) was added to a stirred solution of $\text{Ta}(\text{CHCMe}_3)(\text{DIPP})_3(\text{THF})$ (0.500 g, 0.58 mmol) in ether (20 mL) at room temperature. After 4.5 h the solution was filtered through Celite, and the solvent was removed from the filtrate in vacuo. The resulting yellow oil was dissolved in pentane, and the solution was cooled to -30°C to give yellow crystals (0.242 g, 43%): ^1H NMR δ 7.04 (6, H_m), 6.91 (3, H_p), 3.99 (1, H_α), 3.64 (6, CHMe_2), 1.24 and 1.23 (each 18, CHMe_2), 0.97 (9, CMe_3), 0.39 and -0.09 (each 9, SiMe_3); ^{13}C NMR δ 254.8 (s, C_α), 232.2 (s, C_β), 157.4 (C_{ipso}), 137.9 (C_α), 123.7 (C_m), 123.2 (C_p), 59.9 (d, $\text{J}_{\text{CH}} = 116$, C_α), 35.1 (CMe_3), 31.5 (CMe_3), 27.6 (CHMe_2), 25.5 (CHMe_2), 2.27 and 1.95 (each SiMe_3). Anal. Calcd for $\text{TaC}_{49}\text{H}_{79}\text{O}_3\text{Si}_2$: C, 61.74; H, 8.35. Found: C, 61.85; H, 8.25.

$\text{Ta}[\text{C}(\text{SiMe}_3)\text{C}(\text{SiMe}_3)\text{CH}(\text{CMe}_3)](\text{DIPP})_3(\text{py})$ (**3b**). Pyridine (17 μL , 0.21 mmol) was added via syringe to a stirred solution of $\text{Ta}[\text{C}(\text{SiMe}_3)\text{C}(\text{SiMe}_3)\text{CHCMe}_3](\text{DIPP})_3$ (0.050 g, 0.05 mmol) in ether (5 mL) at room temperature. The solution was stirred for 75 min, during which time no color change was observed. The solution was filtered through Celite and the solvent removed from the filtrate in vacuo to give a yellow oil virtually quantitatively (by ^1H NMR): ^1H NMR δ 8.53 (2, py H_α), 7.05 (6, H_m), 6.96 (unresolved, 2, py H_m), 6.91 (3, H_p), 6.63 (1, py H_p), 3.99 (1, H_α), 3.64 (6, CHMe_2), 1.24 and 1.23 (each 18, CHMe_2), 0.97 (9, CMe_3), 0.39 and -0.09 (each 9, SiMe_3). Repeated attempts to obtain the compound in pure crystalline form failed.

$\text{Ta}[\text{CH}_2\text{C}(\text{Me})\text{C}(\text{CHCMe}_3)](\text{DIPP})_3$ (**4a**). 2-Methylbut-1-en-3-yne (32 μL , 0.33 mmol) was added to a stirred solution of $\text{Ta}(\text{CHCMe}_3)(\text{DIPP})_3(\text{THF})$ (0.280 g, 0.33 mmol) in ether (10 mL) at -30°C . After 20 min the orange solution was filtered through Celite and the solvent removed in vacuo to yield an extremely pentane-soluble orange oil. Repeated attempts to obtain the compound in pure crystalline form failed. The yield is virtually quantitative by ^1H NMR: ^1H NMR δ 7.07 (6, H_m), 6.94 (3, H_p), 6.77 (d, 1, $\text{J}_{\text{HH}} = 16$, CHCHCMe_3), 5.43 (d, 1, $\text{J}_{\text{HH}} = 16$, CHCHCMe_3), 3.57 (6, CHMe_2), 2.20 (3, $\beta\text{-CMe}$), 2.15 (s, 2, $\alpha\text{-CH}_2$), 1.21 (36, CHMe_2), 0.83 (9, CMe_3); ^{13}C NMR δ 216.9 (C_α), 156.8 (C_{ipso}), 150.5 (C_β), 145.6 (d, $\text{J}_{\text{CH}} = 150$, CHCHCMe_3), 138.4 (C_α), 124.9 (d, $\text{J}_{\text{CH}} = 149$, CHCHCMe_3), 123.6 (C_m and C_p), 57.3 (t, $\text{J}_{\text{CH}} = 141$, C_α), 33.1 (CMe_3), 29.7 (CMe_3), 27.5 (CHMe_2), 24.0 (CHMe_2), 20.1 (C_βMe).

$\text{Ta}[\text{CH}_2\text{C}(\text{Me})\text{C}(\text{CHCMe}_3)](\text{DIPP})_3(\text{py})$ (**4b**). A solution of 2-methylbut-1-en-3-yne (46 μL , 0.47 mmol) in ether (5 mL) at -30°C was added to a stirred solution of $\text{Ta}(\text{CHCMe}_3)(\text{DIPP})_3(\text{THF})$ (0.400 g, 0.47 mmol) in ether (10 mL at -30°C). After 1 h pyridine (140 μL , 1.74 mmol) was added to the orange

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solution. After 1 h the solvent was removed in vacuo to yield a light orange oil. Light orange crystals were obtained from pentane at $-30\text{ }^{\circ}\text{C}$ (0.227 g, 52%): $^1\text{H NMR}$ δ 8.64 (br d, 2, py H_o), 7.09 (6, H_m), 6.92 (3, H_p), 6.78 (1, py H_p), 6.27 (br, 3, CHCHCMe_3 and py H_m), 5.18 (d, 1, $J_{\text{HH}} = 16$, CHCHCMe_3), 3.55 (6, CHMe_2), 2.26 (3, C_αMe), 1.76 (2, $\alpha\text{-CH}_2$), 1.10 (36, CHMe_2), 0.89 (9, CMe_3); $^{13}\text{C NMR}$ δ 212.8 (C_α), 157.1 (C_{ipso}), 149.8 (py C_o), 148.2 (C_β), 139.8 (unresolved, CHCHCMe_3), 138.5 (C_α), 137.7 (unresolved, py C_p), 127.1 (unresolved, CHCHCMe_3), 124.7 (unresolved, py C_m), 123.9 (C_m), 122.2 (C_p), 56.7 (t, $J_{\text{CH}} = 140$, C_α), 33.0 (CMe_3), 30.1 (CMe_3), 27.0 (CHMe_2), 24.5 (CHMe_2), 20.3 (C_βMe). Anal. Calcd for $\text{TaC}_{51}\text{H}_{72}\text{NO}_3$: C, 66.00; H, 7.82; N, 1.51. Found: C, 65.81; H, 7.99; N, 1.29.

Ta[C(Me)C(Me)CHCMe₃](DIPP)₃(py) (5). A solution of 2-butyne (37 μL , 0.47 mmol) in ether (10 mL at $-30\text{ }^{\circ}\text{C}$) was added to a stirred solution of $\text{Ta}(\text{CHCMe}_3)(\text{DIPP})_3(\text{THF})$ (0.400 g, 0.47 mmol) in ether (10 mL) at $-30\text{ }^{\circ}\text{C}$. The solution rapidly turned orange. The solution was stirred at room temperature for 30 min and recooled to $-30\text{ }^{\circ}\text{C}$, and pyridine (113 μL , 1.40 mmol) was added. The solution immediately turned very dark. The solution was warmed to room temperature and after 20 min was filtered through Celite. The solvent was removed from the filtrate in vacuo, and the resulting almost black residue was dissolved in pentane. Cooling this solution to $-30\text{ }^{\circ}\text{C}$ gave deep purple crystals (0.330 g, 77%): $^1\text{H NMR}$ δ 8.49 (br d, 2, py H_o), 7.06 (6, H_m), 6.92 (3, H_p), 6.9–6.7 (br, 1, py H_p), 6.55 (br, 2, py H_m), 3.64 (6, CHMe_2), 2.08 (3, C_βMe), 1.21 (36, CHMe_2), 1.15 (9, CMe_3). The α -methyl group and olefinic H resonances were not observed in the room-temperature spectrum, due to a fluxional process that interconverts the alkylidene and the corresponding metallacyclobutene complexes: $^1\text{H NMR}$ (toluene- d_8 , $-60\text{ }^{\circ}\text{C}$) δ 8.64 and 8.22 (each a d, 2, py H_o), 7.2–6.7 (m, H_m and H_p and CHCMe_3), 6.57 (s, ~ 0.33 , CHCMe_3), 6.26 (t, 1, py H_p), 5.98 (t, 2, py H_m), 4.34 and 4.18 (each a s, 3, C_αMe), 4.05 and 3.57 (br, 6, CHMe_2), 2.24 (s, 3, C_βMe), 1.4–1.1 (br, CHMe_2 and CMe_3); $^{13}\text{C NMR}$ δ 157.4 (C_{ipso}), 150.3 (py C_o), 138.3 (C_α), 136.4 (py C_p), 124.0 and 123.7 (C_p and C_m), 122.9 (py C_m), 33.4 (CMe_3), 27.2 (CHMe_2), 24.5 (CHMe_2), 23.9 and 20.4 (C_αMe and C_βMe). The C_α , C_β , and C, resonances were not observed in the room temperature spectrum, due to a fluxional process that interconverts the alkylidene and the corresponding metallacyclobutene complexes. The CMe_3 resonance was also not observed. $^{13}\text{C NMR}$ (toluene- d_8 , $-60\text{ }^{\circ}\text{C}$, 75.4 MHz): δ 256.4 and 232.1 (C_α). Anal. Calcd for $\text{TaC}_{50}\text{H}_{72}\text{O}_3\text{N}$: C, 65.54; H, 7.94. Found: C, 65.38; H, 7.97.

Ta[C(Ph)C(Ph)CHCMe₃](DIPP)₃(py) (6). Pyridine (75 μL , 0.93 mmol) was added to a stirred solution of $\text{Ta}[\text{C}(\text{Ph})\text{C}(\text{Ph})\text{CH}(\text{CMe}_3)](\text{DIPP})_3$ (0.165 g, 0.17 mmol) in ether (10 mL) at room temperature. The solution quickly turned dark purple. After 30 min the solution was filtered through Celite, and the solvent was removed from the filtrate in vacuo. The resulting dark oil was dissolved in pentane, and the solution was cooled to $-30\text{ }^{\circ}\text{C}$ to yield dark purple crystals (0.085 g, 47%): $^1\text{H NMR}$ δ 8.54 (br, 2, py H_o), 7.47–6.73 (12, phenyl resonances, py H_p , and CHCMe_3), 7.05 (6, H_m), 6.93 (3, H_p), 6.58 (br, 2, py H_m), 3.67 (br septet, 6, CHMe_2), 1.14 (36, CHMe_2), 1.10 (9, CMe_3); $^{13}\text{C NMR}$ δ 243.1 (C_α), 157.2 (C_{ipso}), 150.3 (py C_o), 143.9 (phenyl C_{ipso} 's), 138.7 (C_α), 135.8 (py C_p), 130.2–122.0 (unresolved), 124.0 (C_m and C_p), 39.0 (CMe_3), 34.1 (CMe_3), 27.5 (CHMe_2), 24.6 (CHMe_2). Anal. Calcd for $\text{TaC}_{60}\text{H}_{76}\text{NO}_3$: C, 69.27; H, 7.38. Found: C, 69.23; H, 7.56.

Ta[C(Me)C(Me)C(Me)CH₂CMe₃](DIPP)₃ (8). A solution of 2-butyne (69 μL , 0.88 mmol) in ether (5 mL at $-30\text{ }^{\circ}\text{C}$) was added to a stirred solution of $\text{Ta}[\text{C}(\text{Me})\text{C}(\text{Me})\text{CHCMe}_3](\text{DIPP})_3(\text{py})$ (0.800 g, 0.87 mmol) in ether (15 mL) at $-30\text{ }^{\circ}\text{C}$. The solution turned orange-red. After 20 min the solution was filtered through Celite, and the solvent was removed from the filtrate in vacuo to give a deep red oil virtually quantitatively. A red precipitate could be obtained by cooling a concentrated pentane solution to $-30\text{ }^{\circ}\text{C}$ (0.365 g, 47%); light orange crystals were obtained by slow recrystallization from pentane at $-40\text{ }^{\circ}\text{C}$: $^1\text{H NMR}$ δ 7.08 (6, H_m), 6.96 (3, H_p), 3.44 (6, CHMe_2), 2.91 (s, 2, $\alpha\text{-CH}_2$), 2.51 (s, 2, CH_2CMe_3), 2.19 (s, 3, $\alpha\text{-CMe}$), 2.12 and 1.74 (each 3, $\beta\text{-CMe}$ and $\text{CMeCH}_2\text{CMe}_3$), 1.18 (36, CHMe_2), 0.98 (9, CMe_3); $^{13}\text{C NMR}$ δ 214.0 (C_α), 158.7, 148.9, and 129.2 (C_β 's and $\text{CMeCH}_2\text{CMe}_3$), 156.9 (C_{ipso}), 138.4 (C_α), 123.6 (C_m and C_p), 82.3 (t, $J_{\text{CH}} = 119$, $\alpha\text{-CH}_2$), 47.5 (t, $J_{\text{CH}} = 124$, CH_2CMe_3), 33.1 (CMe_3), 32.2 (CMe_3), 27.6 (CHMe_2), 25.2, 20.0, and 18.5 (each a C_β), 24.0

(CHMe_2). Anal. Calcd for $\text{TaC}_{49}\text{H}_{73}\text{O}_3$: C, 66.05; H, 8.26. Found: C, 65.79; H, 8.12.

Preparation of Poly(2-butyne) Employing 5, 8, c Ta-(CHCMe₃)(TIPT)₃(THF). Standard solutions of 2-butyne in toluene (prepared and stored at $-30\text{ }^{\circ}\text{C}$, $\sim 2.5\text{ M}$) were employed. In a typical reaction, 100 equiv of 2-butyne in toluene (5 mL at $-30\text{ }^{\circ}\text{C}$) were added to a stirred solution of **5** (25 mg) in toluene (10 mL at $-30\text{ }^{\circ}\text{C}$). The reaction solution was warmed to room temperature and stirred for 30 min. The polymer was cleaved from the metal by addition of excess ($\sim 50\text{ } \mu\text{L}$) benzaldehyde. The solvent was removed in vacuo to give a rubbery colorless residue in quantitative yield. The poly(2-butyne) can be dissolved in toluene or, with more difficulty, methylene chloride. Before GPC analysis the polymer solution is passed through alumina to remove any remaining metal complexes.

Higher molecular weight samples (150–200 equiv of 2-butyne) dissolve incompletely in methylene chloride, even with heating. Decreased solubility of higher molecular weight samples (especially in methylene chloride) is consistent with the general insolubility noted for symmetrically substituted polyacetylenes.² Incomplete dissolution is not thought to arise from the presence of other higher molecular weight species, since GPC analysis shows the dissolved fraction to be essentially monodisperse. If the reaction of **5** with 2-butyne were to produce polymers with a range of molecular weights, some of which would not be soluble, then GPC analysis of the soluble fraction would be expected to show a distribution of molecular weights up to the molecular weight where the polymer is no longer sufficiently soluble (and therefore absent in the chromatogram). However, molecular weights of the polymers increase linearly with the number of equivalents of 2-butyne added, even when samples have not completely dissolved, and no "cutoff" molecular weight is observed. Furthermore, the solubility of the higher molecular weight poly(2-butyne) samples in methylene chloride is enhanced significantly upon addition of a small amount of toluene, and the resulting GPC chromatograms (run in methylene chloride) are identical with those obtained by using only methylene chloride.

Preparation of poly(2-butyne) from **8** and $\text{Ta}(\text{CHCMe}_3)(\text{TIPT})_3(\text{THF})$ was performed in a manner analogous to that described above for **5**, except in the case of **8** 2 equiv of pyridine was added to the solution of **8** in toluene before addition of 2-butyne. These reactions occur readily at room temperature (100 equiv of 2-butyne are consumed within 60 min).

Preparation of Polynorbornene and Poly(2-butyne)/Polynorbornene Block Copolymers Employing 5. For polymerization of NBE by **5**, 100 equiv of NBE in toluene (5 mL at $-30\text{ }^{\circ}\text{C}$) was added to a solution of **5** (20 mg) in toluene (10 mL at $-30\text{ }^{\circ}\text{C}$) to give a colorless solution indicative of metallacyclobutane formation. The reaction mixture was heated to $65\text{ }^{\circ}\text{C}$ for 2 h. After all NBE was consumed the solution turned light yellow. Benzaldehyde was then added. The reaction was then kept at $65\text{ }^{\circ}\text{C}$ for an additional 15 min. The solvents were removed in vacuo. The colorless polynorbornene was rinsed with methanol and dissolved in methylene chloride. The methylene chloride solution was filtered through alumina in order to remove any remaining metal complexes in preparation for GPC analysis.

Block copolymers were prepared by adding 2-butyne to **5** followed by NBE or by adding NBE to $\text{Ta}[\text{CH}(\text{C}_5\text{H}_9)\text{CHCHCMe}_3](\text{DIPP})_3$ followed by pyridine and 2-butyne. In the first procedure a solution of 2-butyne in toluene (5 mL at $-30\text{ }^{\circ}\text{C}$) was added to a rapidly stirred solution of **5** ($\sim 25\text{ mg}$) in toluene (10 mL at $-30\text{ }^{\circ}\text{C}$). The reaction was warmed to room temperature, and after allowing sufficient time for all 2-butyne to be consumed, it was recooled to $-30\text{ }^{\circ}\text{C}$, and an aliquot was removed for GPC analysis. A solution of NBE in toluene (5 mL at $-30\text{ }^{\circ}\text{C}$) was then added to the bulk reaction solution with rapid stirring. The reaction solution was heated to $65\text{ }^{\circ}\text{C}$ until all NBE was consumed. Benzaldehyde ($\sim 50\text{ } \mu\text{L}$) was then added. After $\sim 15\text{ min}$ the solvent was removed in vacuo leaving a colorless polymer. The polymer was rinsed with methanol and dissolved in methylene chloride or toluene, and the solution was filtered through alumina in preparation for GPC analysis.

In the second procedure a solution of NBE in toluene (5 mL at $-30\text{ }^{\circ}\text{C}$) was added to a solution of $\text{Ta}[\text{CH}(\text{C}_5\text{H}_9)\text{CHCHCMe}_3](\text{DIPP})_3$ ($\sim 25\text{ mg}$) in toluene (10 mL at $-30\text{ }^{\circ}\text{C}$). The reaction solution was heated to $65\text{ }^{\circ}\text{C}$ in order to polymerize

the NBE.¹⁸ An aliquot was removed for GPC analysis, and pyridine (3 equiv) was added to the remaining solution at 65 °C. A solution of 2-butyne in toluene (5 mL) was then added to the reaction solution at 65 °C in a closed system (so no 2-butyne would be lost). After 15 min benzaldehyde (~50 μL) was added, and the solvent was removed in vacuo. The polymer was rinsed with methanol, dissolved in methylene chloride, and filtered through alumina in preparation for GPC analysis.

Preparation of Poly(1-pentyne) Employing 5 or Ta(CHCMe₃)(TIPT)₃(THF). These reactions were performed as described above for the polymerization of 2-butyne. Polymer samples of poly(1-pentyne) are deep orange and oily. All samples dissolve readily in common organic solvents. (Polyacetylenes that are not symmetrically substituted are known to be more soluble.)

X-ray Structure of Ta[C(Me)C(Me)CHCMe₃](DIPP)₃(py) (5). Crystals of 5 were obtained from pentane at -30 °C. They were found to be of poor quality for X-ray studies, but an adequate one was finally located. A dark purple prismatic crystal having approximate dimensions of 0.50 × 0.30 × 0.40 mm was mounted on a glass fiber under a flow of nitrogen. All measurements were made on a Rigaku AFC6R diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å) and a 12KW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 24 carefully centered reflections in the range $30.00 < 2\theta < 35.01^\circ$, corresponded to a monoclinic cell with dimensions $a = 14.791$ (4) Å, $b = 19.716$ (4) Å, $c = 16.115$ (5) Å, $V = 4668$ (4) Å³, and $\beta = 96.60$ (3)°. For $Z = 4$ and $fw = 916.07$ (TaC₅₀H₇₂O₃N) the calculated density is 1.30 g/cm³. The space group was determined to be $P2_1/n$ (No. 14).

The data were collected at a temperature of -65 ± 1 °C by using the ω -2 θ scan technique to a maximum 2θ value of 55.1°. Of the 11510 reflections which were collected, 11 096 were unique ($R_{\text{int}} = 0.037$). The intensities of three representative reflections which were measured after every 100 reflections remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Mo K α is 25.2 cm⁻¹. An empirical absorption correction^{29a} was applied which resulted in transmission factors ranging from 0.61 to 1.14. The data were corrected for Lorentz and polarization effects.

The structure was solved by the Patterson method. The tantalum atom and its coordination sphere were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions ($d_{\text{C-H}} = 0.95$ Å) and were assigned isotropic thermal parameters 20% greater than the B_{eq} value of the atom to which they were bonded. The final cycle of full-matrix least-squares refinement^{29b} was based on 4992 observed reflections ($I > 3.00\sigma(I)$) and 251 variable parameters and converged (largest parameter shift was 0.02 times its esd) with unweighted and weighted agreement factors of $R = 0.084$ and $R_w = 0.087$; $p = 0.01$. Reflections whose agreements with calculated data based upon $(F_o - F_c)$ were greater than $20\sigma(F_o)$ were omitted. These data most likely suffer from secondary extinction that cannot be refined.

Neutral atom scattering factors were taken from Cromer and Waber.^{30a} Anomalous dispersion effects were included in F_c ;³¹ the value for Δf and $\Delta f''$ were those of Cromer.^{30b} All calculations were performed by using the TEXSAN crystallographic software package of Molecular Structure Corporation, College Station, TX.

X-ray Structure of Ta[C(Me)C(Me)C(CMeCH₂CMe₃)-CH₂](DIPP)₃ (8). A light orange pyramidal crystal (from pentane at -30 °C) having approximate dimensions of 0.25 × 0.30 × 0.30 mm was mounted on a glass fiber under a flow of nitrogen. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo K α radiation ($\lambda =$

0.71069 Å). Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $20.00 < 2\theta < 26.00^\circ$, corresponded to a monoclinic cell with dimensions $a = 10.632$ (4) Å, $b = 12.750$ (9) Å, $c = 34.144$ (9) Å, $V = 4627$ (6) Å³, and $\beta = 91.42$ (3)°. For $Z = 4$ and $fw = 891.06$ (TaC₄₉H₇₃O₃), the calculated density is 1.279 g/cm³. The space group was determined to be $P2_1/c$ (No. 14).

The data were collected at a temperature of -65 ± 1 °C by using the ω -scan technique to a maximum 2θ value of 55.0°. Of the 11 686 reflections collected, 11 089 were unique ($R_{\text{int}} = 0.056$); equivalent reflections were merged. The intensities of three representative reflections which were measured after every 60 min of X-ray exposure time remained constant throughout data collection indicating crystal and electronic stability (no decay correction was applied). The linear absorption coefficient for Mo K α is 25.4 cm⁻¹. An empirical absorption correction^{29a} was applied which resulted in transmission factors ranging from 0.79 to 1.24. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.³² All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions ($d_{\text{C-H}} = 0.95$ Å) and were assigned isotropic thermal parameters which were 20% greater than the B_{eq} value of the atom to which they were bonded. The final cycle of full-matrix least-squares refinement^{29b} was based on 4417 observed reflections ($I > 3.00\sigma(I)$) and 478 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of $R = 0.048$ and $R_w = 0.050$.

The standard deviation of an observation of unit weight was 1.09. The weighting scheme was based on counting statistics and included a factor ($p = 0.05$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin \theta)/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.67 and -1.34 e/Å³, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.^{30a} Anomalous dispersion effects were included in F_c ;³¹ the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.^{30b} All calculations were performed by using the TEXSAN crystallographic software package.

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Registry No. 1, 118419-64-0; 2, 118419-65-1; 3a, 118419-66-2; 3b, 118419-71-9; 4a, 118419-67-3; 4b, 118419-72-0; 5, 118419-68-4; 6, 118419-69-5; 8, 118419-70-8; Ta(CHCMe₃)(DIPP)₃(THF), 106034-24-6; 2-butyne, 503-17-3; diphenylacetylene, 501-65-5; bis(trimethylsilyl)acetylene, 14630-40-1; 2-methyl-buten-3-yne, 78-80-8; pyridine, 110-86-1; 2-butyne (homopolymer), 25684-85-9; poly(1-pentyne), 28904-75-8; (2-butyne) (norbornene) (copolymer), 118419-63-9; polynorbornene, 25038-76-0.

Supplementary Material Available: Tables of final positional parameters, intramolecular distances involving the non-hydrogen atoms, intramolecular bond angles involving the non-hydrogen atoms, and anisotropic thermal parameters for 5 and 8 (36 pages); listings of observed and calculated structure factors for 5 and 8 (105 pages). Ordering information is given on any current masthead page.

(29) (a) Walker, N.; Stuart, D. *Acta Crystallogr.* 1983, A39, 158. (b) Least-squares function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2 / \sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2] / Lp^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz-polarization factor, and p = p factor.

(30) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.2 A. (b) Table 2.3.1.

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(32) Structure solution methods: PHASE: Calabrese, J. C.; PHASE—Patterson Heavy Atom Solution Extractor; Ph.D. Thesis, University of Wisconsin—Madison, 1972. DIRDIF: Beurskens, P. T. Direct Methods for Difference Structures—an automatic procedure for phase extension and refinement of difference structure factors; Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed Nijmegen, Netherlands.