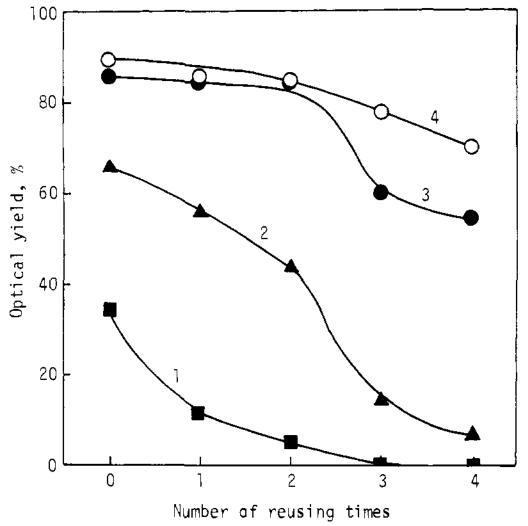

Figure 2. Electrochemical asymmetric oxidation of *tert*-butyl phenyl sulfide (**1e**) to the corresponding sulfoxide (**2e**) on reused poly(L-valine)-coated platinum electrodes. Each electrode was repeatedly reused passing 2.0 F mol^{-1} of charge for each electrolysis in electrolytic solution containing 1% water at a constant current density of 0.3 A dm^{-2} at 0 °C: (1) A_{11} electrode coated in 0.5% w/v coating solution, (2) B_{11} electrode coated in the same, (3) C_{11} electrode coated in the same, (4) C_{11} electrode recoated in 0.25% w/v fresh solution before each electrolysis.

An additional improvement of the durability of the C_{11} electrode in repeated reuse could be made by recoating the electrode in a fresh poly(L-valine) solution after it is rinsed out in trifluoroacetic acid. The durability was somewhat improved by this way and the asymmetry inducing power decreased more slightly with the increase of reusing times, as shown in Figure 2 (curve 4). Such a small decrease of the power may be due to damage of the polypyrrole layer.

Experimental Section

Materials. Sulfide **1a** was commercially supplied from Tokyo Kasei Co. Sulfides **1b–e** and **1f,g** were prepared by the methods of Ipatieff et al.[32] and Zavgorodnii,[33] respectively, and confirmed by boiling point, IR, and MS data.

Poly(amino acid)s (poly(L-valine), poly (γ-benzyl L-glutamate), and poly(L-leucine)) were prepared from the corresponding optically pure amino acids by a method described in our earlier reports.[23,24] Their molecular weights were not known except for poly(L-valine) (ca. 2000[23]).

Poly (amino acid)-Coated Electrodes. The coated electrodes used in this work were prepared by methods similar to those described previously[29] for the preparation of poly(L-valine)-coated platinum electrodes.[30] Before coating, graphite plates were polished with fine emery paper, washed with ethanol, and dried at room temperature.

Electrolysis. The electrolytic oxidation of sulfides was carried out in 0.1 M n-Bu_4NBF_4/acetonitrile (containing water) by a potentiostatic method. Details of typical electrolytic conditions and procedures were given in the previous report.[29]

Product Analysis. After the electrolysis, the anodic solution was evaporated and then extracted with chloroform. Sulfoxides **2a** and **2b–g** were purely separated from the chloroform extracts by gas chromatography (Triton X305, 200 °C) and column chromatography (Kieselguhr 60), respectively. Eluents for the column chromatography were chloroform (for **2b,d,e**) and chloroform–ethyl acetate (1:1 v/v for **2c**; 9:1 v/v for **2f,g**). The sulfoxides separated thus were confirmed by IR and MS data.

Any products (e.g., sulfones) other than the sulfoxides could not be separated. Oxygen evolution was observed during the electrolysis. Unreacted sulfides were recovered in some cases where chemical yields of the sulfoxides were estimated on the basis of the sulfides consumed.

Optical Yields. Optical rotation of the sulfoxides separated was measured in 1–10-cm photocells of a highly sensitive polarimeter (Union Co. automatic polarimeter, Model PM-101). The optical yields of **2a–e** were calculated with reference to $[\alpha]_D$ values reported for the optically pure enantiomers: $[\alpha]^{20}_D$ + 146.2° (c 1.76, ethanol)[11] for (R)-**2a**, $[\alpha]^{25}_D$ + 169.9° (c 1.6, acetone)[18] for (R)-**2b**, $[\alpha]^{25}_D$ + 178.9° (c 2.0, ethanol)[18] for (R)-**2c**, $[\alpha]^{25}_D$ −237.3° (c 2.0, ethanol)[18] for (S)-**2d**, and $[\alpha]^{25}_D$ + 180.0° (c 2.0, ethanol)[11] for (R)-**2e**. Optical rotation of **2f,g** was also measured in acetonitrile. However, their optical yields were calculated not from their optical rotating powers but from NMR spectra measured in chloroform-d in the presence of tris[3-[(trifluoromethyl)hydroxymethylene]-d-camphorato]europium(III) as an enantiomer-shift reagent. On the basis of the optical rotation and the NMR spectra, we concluded that optically pure **2f** and **2g** have $[\alpha]^{20}_D$ 196.7° (c 2.0, acetonitrile) and $[\alpha]^{20}_D$ 190.0° (c 2.0, acetonitrile), respectively.[34]

Registry No. **1a**, 100-68-5; **1b**, 3019-20-3; **1c**, 1126-80-3; **1d**, 13307-61-4; **1e**, 3019-19-0; **1f**, 7570-92-5; **1g**, 3699-01-2; **2a**, 18453-46-8; **2b**, 80225-50-9; **2c**, 77448-93-2; **2d**, 72174-22-2; **2e**, 62076-10-2; **2f**, 89066-10-4; **2g**, 89066-11-5; poly(L-valine), 25609-85-2; poly(L-leucine), 25248-98-0; poly(γ-benzyl L-glutamate), 25014-27-1; platinum, 7440-06-4; graphite, 7782-42-5; polypyrrole, 30604-81-0.

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[34] Relations between the optical rotating powers and optical purities indicated straight lines that coincided the origin.

Polymerizations of Acetylenes and Cyclic Olefins Induced by Metal Carbynes

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New York, New York 10027. *Received August 15, 1983*

Abstract: *trans*-Bromotetracarbonyl(phenylmethylidyne)tungsten and related metal carbynes induce acetylenes and cycloalkenes to polymerize. The acetylenes include examples that are monosubstituted, disubstituted, and unsubstituted, as well as the first reported functionalized acetylenes in which the functional groups (the nitrile, ester, and halogen functions were studied) are not attached to the triple bond. The cycloalkenes yield polyalkenamers whose double bonds are largely cis. This last polymerization is speeded by the presence of oxygen. The stereochemistries of the polyacetylenes and the polynorbornenamer produced when the initiator is the metal carbyne are similar to those of the polymers produced when the initiator is pentacarbonyl(methoxyphenylmethylene)tungsten. A possible mechanism is presented to account for why the metal carbynes behave as though they were sources of reactive metal carbenes.

Ideas about the mechanism of the metal-catalyzed metathesis of olefins[1] suggested that isolable metal carbenes might initiate such reactions, as indeed turned out to be true, as Casey's pentacarbonyl(diphenylmethylene)tungsten[2] (**1**) initiating metatheses

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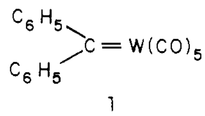
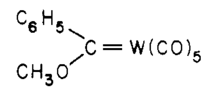


1



2

of a variety of olefins[3] and Fischer's pentacarbonyl(methoxyphenylmethylene)tungsten[4] (**2**) initiating those of olefins whose double bonds are strained.[5,6] Similar ideas about the metal-catalyzed metatheses of acetylenes[1a,11] in turn suggested that isolable metal carbynes might initiate acetylene metatheses, but as is seen below, the archetypical metal carbyne of E. O. Fischer, *trans*-bromotetracarbonyl(phenylmethylidyne)tungsten (**3**),[12] is not effective in doing this. Schrock's tri-*tert*-butoxy(neopentylidyne)tungsten (**4**), however, is,[13] and this discovery, spectacular when viewed in almost any way, is interesting to consider in its contrast to this background.

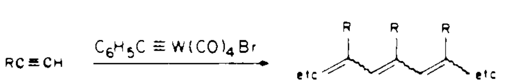
$$C_6H_5C\equiv W(CO)_4Br$$

3

$$(CH_3)_3CC\equiv W[OC(CH_3)_3]_3$$

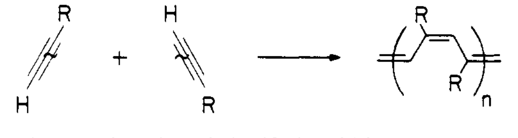
4

The Fischer metal carbyne **3** and related derivatives do not, however, leave acetylenes unchanged. As demonstrated below, they cause acetylenes to polymerize, giving soluble, structurally homogeneous polymers in accord with eq 1. And they do this not only to various simple monosubstituted acetylenes whose polymerization can be brought about by a number of initiators,[14-16] but also to acetylenes polymerized previously by only few or no initiators: disubstituted acetylenes,[18] unsubstituted acetylene (regrettably in this case giving, as do all other effective initiators, only insoluble polymers),[14a,15,19,20] and acetylenes with functional groups remote from the triple bond.[21] (Polymers of these last materials had not previously been prepared.)



(1)

If we suppose that the acetylene polymerization is an olefin metathesis[17,23,24]—that is, that it involves the formal transformation summarized in eq 2—then the ability of a metal derivative to initiate the reaction should signify its ability to generate metal carbenes. It would mean that the metal carbynes that initiate polymerizations of acetylenes might also cause olefins to metathesize, and experiments demonstrating this too are recorded below. The theory also suggests that if metal carbynes are sources of metal carbenes, related metal carbynes and carbenes should



(2)

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(6) Kroll and Doyle were the first to discover that isolable metal carbenes could be important components of effective olefin metathesis catalysts.[7a] They found that ionic metal carbenes plus organoaluminum halides or neutral metal carbenes plus ammonium salts and organoaluminum compounds initiate the reaction. (See also ref 7b.) Chauvin et al. made the significant discovery,[7c,d] which Banasiak recently generalized,[7e] that neutral metal carbenes plus simple metal halides that are Lewis acids devoid of carbon–metal bonds are effective. Banasiak also found that metal carbenes plus organotin compounds work if an organic halide is also present.[7f] Dolgoplosk showed long ago that mixtures plausibly generating metal carbenes initiate olefin metatheses.[8] Osborn et al. recently reported some elegant versions of such experiments.[9] Schrock et al. have recently also prepared metal carbenes that exhibit at least some ability to metathesize olefins.[10]

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(20) Recently units of polyacetylene in soluble form have been obtained by grafting them to soluble polymers [Bates, F. S.; Baker, G. L. *Macromolecules* **1983**, *16*, 704.]

(21) Cyanoacetylene with bases has given low molecular weight polymers.[22a-c] With chromium or cobalt acetylacetonates plus triethylaluminum it gave low yields of only partly soluble polymers[22d] and with titanium tetrachloride[22d] or butoxide[22e] plus triethylaluminum gave low yields of insoluble polymers. Dicyanoacetylene with bases also gave very small polymers.[22f] Methyl propiolate has been polymerized by triethylamine,[22a] by a palladium derivative,[22g] and by $MoCl_5$.[22h] Propiolic acid has been polymerized also, by the chlorides of Mo, Pd, Rh, and Ru.[22h] Acetylenedicarboxylic acid and phenylpropiolic acid have been polymerized by $MoCl_5 + (C_6H_5)_4Sn$[22h] and phenylchloroacetylene by photolyzed $Mo(CO)_6$ in CCl_4.[22i] Propargyl derivatives, $HC\equiv CCH_2X$, where X is Cl and OH, have been polymerized by palladium chloride[22j] and the chloride by photolyzed $W(CO)_6$.[22k] We have been unable to find other polymers of functionalized acetylenes.

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Table I. Yields and Molecular Weights of Polyacetylenes Obtained by Combining Various Acetylenes with the Initiator $C_6H_5C{\equiv}W(CO)_4Br$ at Ambient Temperature (ca. 22 °C)[a]

expt	acetylene	[acetylene]/[initiator]	time, h	yield, %[b]	$10^{-3}\bar{M}_w$[c]	$10^{-3}\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$
1	$C_6H_5C{\equiv}CH$	212	3.0	10	151.0	55.0	2.8
2	$C_6H_5C{\equiv}CH$	210	14.0	63			
3	$CH_3C{\equiv}CH$	380	8.0	52	14.4	5.9	2.4
4	$(CH_3)_3CC{\equiv}CH$	190	3.0	26			
5	$(CH_3)_3CC{\equiv}CH$	190	48.0	39	180.0	70.1	2.6
6	$n\text{-}C_4H_9C{\equiv}CH$	200	48.0	64	120.0	49.0	2.4
7	$CH_3C{\equiv}CC_2H_5$	209	20.0	20	296.0	174.0	1.7
8	$CH_3C{\equiv}CCH_3$	350	19.0	12[d]			
9	$HC{\equiv}CH$	536	92.0	34			
10	$HC{\equiv}C(CH_2)_3Cl$	218	2.5	53	201.0	67.0	3.0
11	$HC{\equiv}C(CH_2)_3CO_2CH_3$	147	38.0	16	14.0	5.8	2.4
12	$HC{\equiv}C(CH_2)_3CN$	80	48.0	16	10.1	3.7	2.7
13	$HC{\equiv}CCH_2OCH_3$	275	e	3	f		
14	$HC{\equiv}CCO_2CH_3$	261	4.0	5	f		

[a] Reactions were effected in evacuated sealed glass tubes. No solvent was used except in the polymerization of acetylene, where 5 mL of xylene was present per g of acetylene. [b] After stirring with $CHCl_3$, precipitating with CH_3OH, and drying under vacuum. [c] Measured by gel-permeation chromatography using tetrahydrofuran solutions, a refractive index monitor, and five Waters Associates μStyragel columns (10^6, 10^5, 10^4, 10^3, and 500 Å). The values recorded are the weights of polystyrens that would exhibit the chromatograms observed. [d] Only part of this is soluble in $CHCl_3$. [e] Two weeks! [f] Almost all insoluble in $CHCl_3$.

induce their substrates to give products that are identical, in particular in stereochemistry. Experiments testing these notions are also described.

Results

Polymerizations of Acetylenes. Table I summarizes experiments testing how effective metal carbyne **3** is as an initiator of acetylene polymerization. For the terminal and internal unfunctionalized acetylenes in lines 1–8 of the table it acts much like the Casey and Fischer metal carbenes (**1** and **2**).[17] Thus, the polymerizations are slow, but they do work well, even when the concentration of the initiator is low. The resulting polymers are tractable, dissolving easily in $CHCl_3$ in 0.5–5 h, except for the polymer of 2-butyne, which dissolves only partially.[25a] The molecular weights are high.[25b]

The structures of the polymers are also clearly defined. The ^1H NMR spectrum of the polypropyne is similar to that of the published spectrum of a sample whose formation was initiated by **1**.[17] Their IR spectra are also similar. (See the supplementary material for the IR spectrum, which is also the same as that of material whose formation was initiated by **2**.) The ^1H NMR spectrum of poly(1-hexyne)[17] and the ^1H and ^{13}C NMR spectra of poly(2-hexyne)[26] and poly(*tert*-butylacetylene) (see Figure 5 in the supplementary material for the ^1H NMR spectrum) match those published.[16a,27,28] They contain no extraneous unidentified peaks. The ^1H NMR spectrum of the poly(phenylacetylene) formed by using the metal carbyne **3** as the initiator (see Figure 3b) resembles one reported recently by Simionescu and Percec for a sample prepared by using the initiator $Co(acac)_3$ plus $(C_2H_5)_3Al$[29a] (acac = acetylacetonate). However, the spectrum of the analogue deuterated in the benzene ring (recorded in the supplementary material in Figure 7b) is cleaner than the corresponding one published by Simionescu and Percec,[29b] for it shows no peak at δ 6.85. The absorption around δ 3.5 seen in some of the spectra in Figure 7 as well as in the spectra of Simionescu and Percec[31] is absent in Figure 7b and also in the full spectrum, which is not displayed, of the undeuterated analogue. The implication (discussed further in the section on stereochemistry) is that the metal carbyne induces the formation of polyphenylacetylene that is structurally purer than that reported before and whose structural and stereochemical purity is exceeded only by that of the sample formed by $MoCl_5$, whose spectrum is displayed in Figure 3a.[32] The metal carbyne also initiates the polymerization of unsubstituted acetylene (line 9 of Table I), and it does this where the Fischer metal carbene fails and the Casey metal carbene is much less effective.[33] The product, a black solid, is, like all previously prepared samples of polyacetylene, insoluble in all solvents tested.[19,20] It was characterized, however, by its ^{13}C NMR spectrum (Figure 6 in the supplementary material), measured on the solid spinning at the magic angle and enhanced by proton–carbon cross polarization.[34] The intense resonance at 138 ppm is characteristic of *trans*-polyacetylene,[35] while smaller peaks at 22 ppm and between 42 and 50 ppm are attributable to saturated impurities.

The metal carbyne also polymerizes the functionalized acetylenes in lines 10–12 in Table I, the first examples of acetylenes polymerizing when these contain functional groups not conjugated with the triple bonds. Propiolic acid and its ester and nitrile derivatives and propargyl alcohol and its derivatives have been polymerized before,[21] but acetylenes in which functional groups are removed from the triple bond have not. In part the reason may be that other initiators have not been tried. Indeed in subsequent research, which will be reported separately,[36] we found other ways to make these polymers, but we also found that other initiators effective for acetylenic hydrocarbons fail with acetylenes that are functionalized. For example, as described in the Experimental Section, the Fischer metal carbene **2** could not substitute for the metal carbyne in bringing about the polymerization of the ester in line 11 of Table I. After 4 days at 45 °C no polymer whatever was obtained.

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[25] (a) Poly(2-butyne) has rarely been obtained in soluble form. See ref 17 and the references cited therein. (b) The molecular weights of the poly(phenylacetylene) are the highest recorded. See ref 23a, 24, and: Sen, A.; Lai, T.-W. *Organometallics* **1982**, *1*, 415.

[26] Highashimura, T.; Deng, Y. -X.; Masuda, T. *Macromolecules* **1982**, *15*, 234.

[27] Okano, Y.; Masuda, T.; Higashimura, T. *Polym. J.* **1982**, *14*, 477.

[28] The ^{13}C NMR spectra of material prepared by using either the metal carbyne **3** or the Fischer metal carbene **2** as the initiator resemble that of polymer whose formation was initiated by $MoCl_5$, Figure 5 in ref 16a and Figure 2 in ref 27, but with small superimposed broader peaks where the olefinic and allylic carbons resonate. These broad resonances are like those of material whose formation was initiated by WCl_6, seen in Figure 1 in ref 27. The spectrum of the material prepared by using **2** as the initiator is much sharper than the one published from our laboratory in ref 17.

[29] (a) Figure 2a in ref 30. (b) Spectrum 1 in Figure 2 in ref 31.

[30] Simionescu, C. I.; Percec, V. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 147.

[31] Simionescu, C. I.; Percec, V. J. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 421.

[32] In contrast to the simplicity of spectra 5a and 7a, the published spectrum of a sample prepared by the same procedure (spectrum 3 in Figure 2 of ref 31) is extremely complex.

[33] The experiments were performed in our laboratory by Van. I. Stuart. The *p*-trifluoromethyl derivative of **2** was used for these experiments.

[34] Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 201.

[35] (a) Maricq et al. (Maricq, M. M.; Waugh, J. S.; MacDiarmid, A. G.; Shirakawa, H.; Heeger, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 7729) report δ 139 (and δ 129 for the cis isomer). (b) Berneir, P.; Schue, F.; Sledz, J.; Roland, M.; Giral, L. *Chem. Scr.* **1981**, *17*, 151, report δ 136.

[36] Ho, T. H.; Katz, T. J., submitted to *J. Mol. Catal.*

Table II. Yields and Molecular Weights of Polyalkenamers Obtained by Combining Cyclic Alkenes with Metal Carbyne Initiators [$C_6X_5C{\equiv}W(CO)_4Br$] under Vacuum

alkene	X	[alkene]/[initiator]	temp, °C	time, h	yield, %[a]	$10^{-3}\overline{M}_w$	$10^{-3}\overline{M}_n$[b]
norbornene	H	267	22	0.08	40.0[c]		
cyclopentene	H	172	22	72.00	5.7		
cyclopentene	Cl	1000	40	24.00	20.0	283	133
cyclooctene	H	178	22	144.00	0.8		
cyclooctene	Cl	250	40	103.00	7.5	97	50

[a] The yields were measured of the materials obtained by dissolving the reaction product in $CHCl_3$ or CH_2Cl_2, precipitating with CH_3OH, and drying under vacuum. [b] Measured by gel permeation chromatography as in Table I. The weights recorded are one-half the weights of polystyrenes that would exhibit chromatograms like those observed (see ref 23c). [c] Only partially soluble in $CHCl_3$ or CH_2Cl_2.

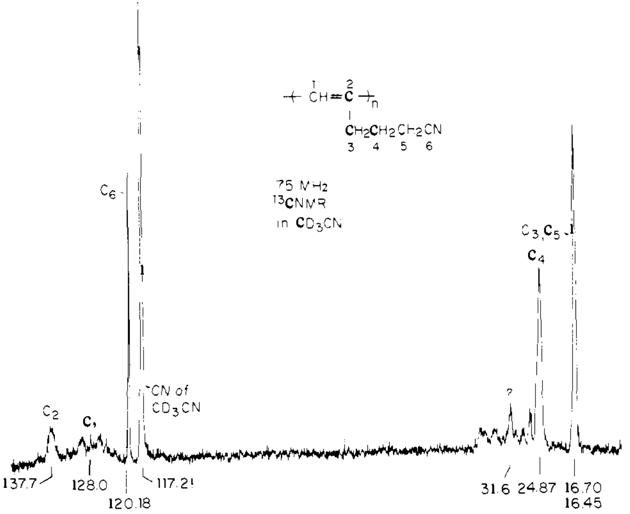


Figure 1. ^{13}C NMR spectrum (5000 scans) of poly(5-cyano-1-hexyne) in CD_3CN. The sample was prepared as in experiment 12, Table I.

The new polymers have been characterized by their ^{13}C NMR spectra, which are summarized in Table VII. To indicate the structural purity of these materials, Figure 1 displays the spectrum of the nitrile, which like the spectra of the other functionalized polymers exhibits small resonances around 32 ppm, possibly attributable to stereoisomeric impurities, but which otherwise shows only the peaks required. (The other ^{13}C NMR spectra are displayed in the supplementary material along with the ^1H NMR spectrum and the IR spectrum of the nitrile.) The functionalized polymers dissolve slowly (ca. 10 h) in THF and $CHCl_3$. The nitrile polymer dissolves much more quickly and well in CH_3CN.

To test a hypothesis described in the Discussion section that the effectiveness of the metal carbyne initiator is associated with the mobility of the halogen atom, the cyclopentadienyl-capped metal carbyne **5**[37] was tested to see if it failed to induce polymerization, which it does. Thus, substituting this derivative for the bromine derivative **3** in the experiment in line 1 of Table I and increasing the reaction time 24-fold (to 3 days) gave at most a 1.6% yield of polymer. In a similar pair of experiments, where the bromo derivative in 6 h gave a 24% yield of polymer, the cyclopentadienyl derivative in 30 days gave at most a 3% yield. Thus, **5** is not an effective initiator.

$C_6H_5C \equiv W(CO)_2(\eta^5\text{-}C_5H_5)$ **5**

$CH_3C \equiv W(CO)_4Br$ **6**

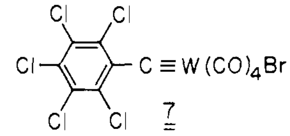
Other halocarbynes related to **3**, however, do initiate the polymerizations, the methylbromocarbyne **6**,[38] for example, inducing propyne to polymerize. (When combined with 333 equiv of the acetylene for 11 days at -15 °C, the methylcarbyne is notably unstable—this metal carbyne gave an 11% yield of polymer.)

Analyses relating to the stereochemistries of the polymers are described later in this paper.

Polymerization of Cyclic Olefins. The acetylene polymerizations described above, although induced by metal carbynes, are, according to the mechanistic hypothesis we have been pursuing, reactions characteristic of metal carbenes. Accordingly, experiments described below were carried out to see whether metal carbynes also induce the more characteristic reaction of metal carbenes, the metathesis of olefins.

Fischer and Wagner reported a number of years[39] ago that the combination methylcarbyne **6** plus titanium tetrachloride is a very efficient initiator for cyclopentene's polymerization, yielding *trans*-polypentenamer, and Kobayashi and Uejima have patented procedures in which the carbyne **3** plus diethylaluminum chloride efficiently polymerize norbornenes, even those like 4-cyanonorbornene that are substituted by functional groups.[40] However, the experiments reported here are the only ones in which metal carbynes without additional cocatalysts have been studied.

Table II records results of some of the experiments in which two metal carbyne initiators, **3** and **7**,[41] were used. The first line of the table shows that **3** initiates norbornene's metathesis, and while this is not surprising in the sense that norbornene is a highly reactive olefin that even dull tungsten compounds can cause to metathesize,[5,42] not all tungsten compounds do in fact succeed. In particular when norbornene was combined with the cyclopentadienyl-capped metal carbyne **5** under the same conditions used in experiment 1 in Table II, no polymer was isolable even after 3 days.



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The other cyclic olefins in Table II are very much less reactive than norbornene, and the polymer yields obtained with the unsubstituted metal carbyne **3** are poor for cyclopentene and miserable for cyclooctene. The problem in part is that since metal carbyne **3** is not thermally stable, the yield cannot be raised by extending the reaction time or by raising the temperature because the initiator decomposes. This is why the pentachloro analogue **7** was studied, as it is known to be more thermally stable.[41] As the table shows, it is, as was hoped, a more effective initiator, giving fair yields of the polymers, ca. 3–9 times as much as the unsubstituted metal carbyne. Experiments described below that use the metal carbyne **6** also accord with this trend, for under reaction conditions similar to those in the table, this thermally less stable

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(37) Fischer, E. O.; Lindner, T. L.; Kreissl, F. R. *J. Organomet. Chem.* **1976**, *112*, C27.

(38) Fischer, E. O.; Kreis, G. *Chem. Ber.* **1976**, *109*, 1673.

(39) Fischer, E. O.; Wagner, W. R. *J. Organomet. Chem.* **1976**, *116*, C21. This paper also states that cyclooctene can be polymerized and that other metal carbynes and other metal chlorides also work.

(40) Kobayashi, M.; Uejima, T. Japanese Patent 77 112 000 Sept 20, 1977; *Chem. Abstr.*, *88* 74 736 h.

(41) Fischer, E. O.; Schwanzer, A.; Fischer, H.; Neugebauer, D.; Huttner, G. *Chem. Ber.* **1977**, *110*, 53.

(42) Oshika, T.; Tabuchi, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 211.

(43) See the references in ref 3a, footnote 18, and Carmen, C. J.; Wilkes, C. E. *Macromolecules* **1974**, *7*, 40. (b) Chen, H. Y. *Appl. Polym. Spectrosc.* **1978**, *7*. (c) Ivin, K. J.; Laverty, D. T.; Rooney, J. J. *Makromol. Chem.* **1977**, *178*, 1545.

Table III. Yields and Molecular Weights of Polyalkenamers Obtained by Combining Cyclic Alkenes C_nH_{2n-2} with $RC{\equiv}W(CO)_4Br$ under Various Conditions under High Vacuum ("V"), in Air ("A"), after Addition of 1 mol of O_2 ("O") or 1 mol of Water ("W") per mol of Metal Carbyne to the Thoroughly Evacuated Reaction Mixture, or in Flasks Superficially Flushed with Nitrogen ("N")[a]

n	R	condn	[alkene]/[metal carbyne]	time, h	yield, %[b]	$10^{-3}\overline{M}_w$	$10^{-3}\overline{M}_n$[c]	% cis	
								IR[d]	^{13}C NMR[e]
8	C_6H_5	V	73	24	0.5				
8	C_6H_5	A	73	24	38.0	240	138	81	78
8	C_6H_5	N	73	60	12.0			92	79 ± 1
8	C_6H_5	O	73	24	16.0				
7	C_6H_5	V	83	24	1.0				
7	C_6H_5	A	83	24	50.0	350	195	84	85 ± 4
7	C_6H_5	O	83	24	26.0			89	
5	C_6H_5	V	172	72	5.7				
5	C_6H_5	O	172	24	82.0	313	184	69	59 ± 2
5	C_6H_5	W	172	144	6.0				
5	C_6H_5	N	200	1	35.0	261	365		
5	C_6H_5	A	256	30	43.0	370	210	71	65 ± 4
5	CH_3	V	250	213	0.3				
5	CH_3	N	226	108	2.0			90	89

[a] Also listed are molecular weights and the fraction of the double bonds that are cis. Reactions were run at ambient temperature (ca. 22 °C) when R was C_6H_5 and at −15 °C when R was CH_3. [b] After dissolving the reaction mixture in $CHCl_3$ or CH_2Cl_2, precipitating the polymer with CH_3OH, and drying it in a vacuum. [c] Measured as described in footnote *b* of Table II. [d] Measured by infrared spectroscopy as described in ref 3a, footnote 16. [e] Measured by the intensities both of the allylic and the olefin carbon resonances which differ for the *E* and *Z* units (see ref 3a, 5, 43). The errors listed are the average deviations of these measurements.

Table IV. Yields of Polyalkenamers Obtained by Combining Cyclic Alkenes C_nH_{2n-2} with Different Halotungsten Tetracarbonyl Phenylalkylidynes, $C_6H_5C{\equiv}W(CO)_4X$, in the Atmosphere at Ambient Temperature[a]

alkene	X	[alkene]/[metal carbyne]	time, h	yield, %[b]	% cis	
					IR[c]	^{13}C NMR[d]
cyclooctene	Cl	66	20	36	75	74 ± 2
cyclooctene	Br	73	24	38	81	78
cyclooctene	I	79	96	5		85 ± 0
cycloheptene	Cl	74	20	35	80	81 ± 1
cycloheptene	Br	81	24	50	84	82 ± 4
cycloheptene	I	87	96	5		90 ± 1
cyclopentene	Cl	163	20	77	73	70 ± 7
cyclopentene	Br	256	30	43	71	65 ± 4
cyclopentene	I	150	20	60		64 ± 4

[a] Stereochemistries and molecular weights are also presented. The three samples with X = Br are the same as the ones in Table III. Their molecular weights are listed in that table. [b] After precipitation from $CHCl_3$ with CH_3OH and drying under vacuum. [c] See Table III, footnote *d*. [d] See Table III, footnote *e*.

metal carbyne[38] is seen to be a bad initiator for cyclopentene's polymerization.

Table III, however, records results that were unanticipated; it shows that the poor yields obtained when the reaction mixtures are thoroughly degassed can be raised to very good yields by simply dispensing with the degassing! The table also shows that the active agent in the air is oxygen, not water.

Although oxygen has been found to cocatalyze a number of olefin metatheses,[44] oxygen inhibits similar reactions initiated by isolable metal carbenes related to the metal carbynes studied here. For example, when 1 mol of oxygen per mol of metal carbene **1** is present, the yield of polypentenamer obtained when cyclopentene is incubated with $^1/_{150}$ mol of **1** for 24 h at 44 °C falls to 0% from 84% in the absence of oxygen.

While the presence or absence of oxygen has a major effect on yields, replacing the bromine atom in the halometal carbyne with chlorine[38] does not. (Replacement with iodine,[38] however, decreases the yields from the less active alkenes.) Table IV summarizes relevant data. This replacement of bromine by chlorine is also without effect if the reactions are performed under vacuum rather than in the atmosphere (although the yields are less). Thus, after 3 days at ambient temperature the chloro analogue of **3** ($^1/_{163}$ mol) polymerized cyclopentene to an extent of 5% (71% cis according to IR or ^{13}C NMR analysis), whereas **3** itself ($^1/_{172}$ mol) gave a 5.7% yield. (In a related experiment the % cis was measured as 74% by IR analysis and 71 ± 3% by ^{13}C NMR.)

However if the bromine atom in **3** (and two carbon monoxides) is replaced by a cyclopentadienyl unit, giving **5**, this material, just

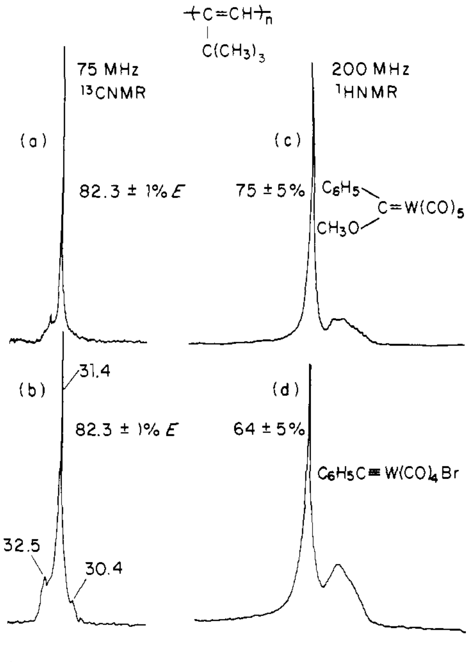

Figure 2. Methyl ^{13}C and olefin ^1H resonances in poly(*tert*-butylacetylene). (a) 75-MHz ^{13}C NMR spectrum of a sample in $CDCl_3$ of poly(*tert*-butylacetylene) prepared by using pentacarbonyl(methoxyphenylmethylene)tungsten (**2**, 0.01 mol per mol of the acetylene) at 40 °C for 36 h and at 60 °C for 6 h (see ref 17). (b) 75-MHz ^{13}C NMR spectrum of a sample (no. 4 in Table I) in $CDCl_3$ of poly(*tert*-butylacetylene) prepared by using the bromocarbyne **3** as the initiator. (c) 200-MHz ^1H NMR spectrum in $CDCl_3$ of the same sample as in Figure 4a. (d) 200-MHz ^1H NMR spectrum in $CDCl_3$ of the same sample as in Figure 4b.

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(44) (a) Basset, J. M.; Ben Taarit, Y.; Coudurier, G.; Praliaud, H. *J. Organomet. Chem.* **1974**, *74*, 167. (b) Basset, J. M.; Coudurier, G.; Mutin, R.; Praliaud, H.; Trambouze, Y. *J. Catal.* **1974**, *34*, 196. (c) Bilhou, J. L.; Basset, J. M. *J. Organomet. Chem.* **1977**, *132*, 395. (d) Amass, A. J.; McGourtey, T. A. *Eur. Polym. J.* **1980**, *16*, 235. Amass, A. J.; Zurimendi, J. A. *Ibid.* **1981**, *17*, 1. (e) Ivin, K. J.; Reddy, B. S. R.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1981**, 1062.

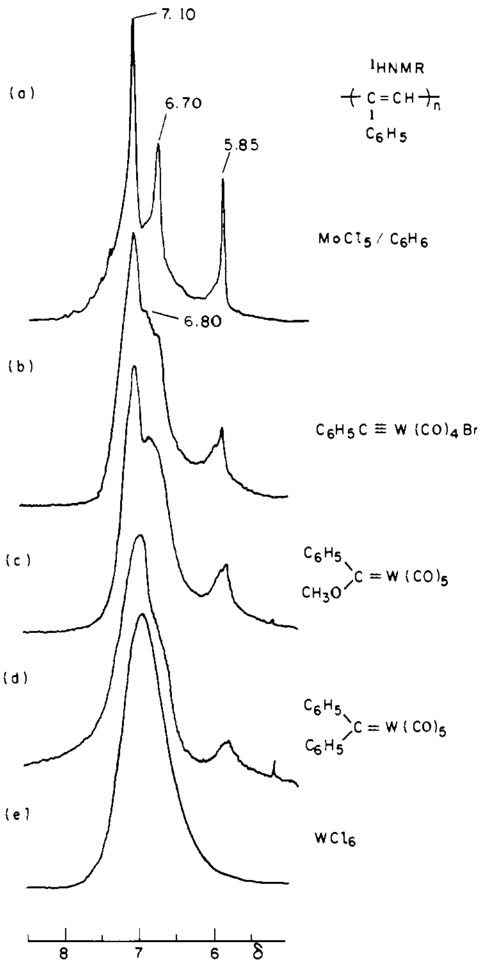

Figure 3. ¹H NMR spectra of poly(phenylacetylenes) (in $CDCl_3$, at 300 MHz for b and c and at 200 MHz for a and d). (a) Polymer made by using $MoCl_5$ (ref 16c and 24) in benzene (ca. 22 °C, 2 h), monomer concentration ([M]) = 2.2 M, initiator concentration ([I]) = 4.4×10^{-2} M. (b) Polymer made by using bromocarbyne **3** as initiator (Table I, Sample 1). (c) Polymer made by using Fischer carbene (**2**) as initiator (ref 17), no solvent, [M]/[I] = 125, 50 °C, 3 h. (d) Polymer made by using Casey's metal–carbene (**1**) as initiator, no solvent, [M]/[I] = 100, 50 °C, 4 h. (e) Polymer made by using WCl_6 (ref 16c and 24) as initiator and CH_2Cl_2 as solvent (ca. 22 °C, $2^{1/2}$ h), [M] = 0.9 M, [I] = 0.9 × 10 M.

as in the experiment with norbornene described above, has no measurable initiating ability in similar experiments. For example, under conditions like those in Table IV, after 96 h cycloheptene (74 mol) in the atmosphere gave no polymer and neither did cyclopentene (170 mol).

Stereochemistries. The data presented in this section appear to show that the stereochemistries of the polymers produced by the metal carbyne initiator **3** and by the related metal carbenes **2** and **1** are similar.

Stereoregularity of Poly(*tert*-butylacetylene). Figure 2 compares the methyl ¹³C nuclear magnetic resonances and the olefin ¹H nuclear magnetic resonances (a full spectrum is in Figure 5 in the supplementary material) of samples of poly(*tert*-butylacetylene) that had been prepared by using bromocarbyne **3** and Fischer carbene **2** as initiators. If the assignment by Masuda et al. of the carbon resonances at 32.5 and 31.4 ppm to *Z* ("trans") and *E* ("cis") units[16a,27] is correct, the intensities of the resonances in Figures 4a,b imply that 82.3 ± 1% of the double bonds in both polymers have the *E* configuration. The ¹H NMR spectrum supports these measurements by displaying two olefin resonances, one that is sharp and intense at δ 6.20 and one that is broad and weaker at δ 5.95. The former peak accounts for 75 ± 5% of the intensity in the case of the polymer prepared by using the Fischer carbene as the initiator and 64 ± 5% of the intensity in the case in which bromocarbyne **3** was the initiator. The presumption is that if the assignment of the ¹³C resonances is correct, the low-field proton resonance is associated with *E* olefin units.

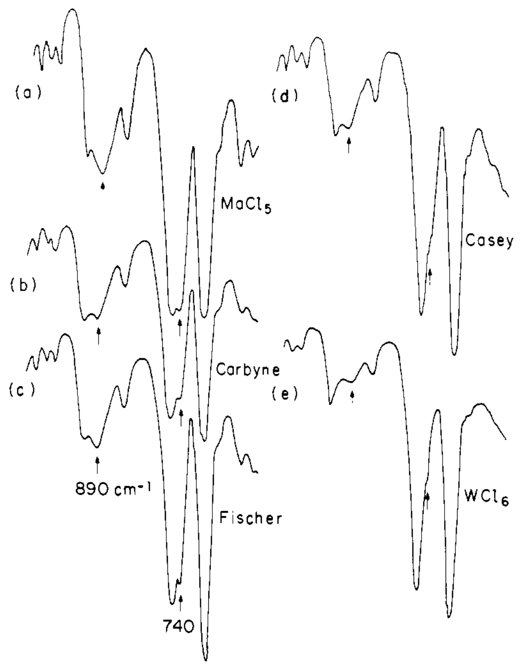

Figure 4. Infrared spectra of poly(phenylacetylene) films. The arrows indicate the position of peaks at 890 and 740 cm⁻¹, which are supposed to be characteristic of units with the *E* configuration. Polymer prepared by using (a) $MoCl_5$, (b) **3**, (c) **2**, (d) **1**, and (e) WCl_6.

Stereoregularity of Poly(phenylacetylene). The ¹H NMR and infrared spectra of samples of poly(phenylacetylene) prepared by using **3** as the initiator are compared in Figures 3 and 4 with the spectra of samples prepared by using other initiators. If as had been supposed[24,25] the peaks in the infrared spectra at 740 and 890 cm⁻¹ measure the concentration of *E* ("cis") units, the fraction of the double bonds having this configuration decreases as the initiator is changed as follows: bromocarbyne (**3**) ≃ $MoCl_5$ ≃ Fischer carbene (**2**) > Casey carbene (**1**) > WCl_6. Simionescu[30,31,45] also assigned the peak at 5.8 ppm in the ¹H NMR spectrum to the olefin resonance of units with the *E* configuration, and following this assignment and the measured intensities, the fraction of the double bonds that are cis is calculated to be 91 ± 15% for polymer made by using bromocarbyne (**3**) and 75 ± 10% for polymer made by using Fischer carbene (**2**). The sample made by using WCl_6 exhibited no peak at δ 5.8, and accordingly, the double bonds are <13 ± 10% cis. The ¹H NMR and infrared spectra of samples of poly(pentadeuteriophenylacetylene) prepared by using bromocarbyne **3** and other initiators were also compared. (See Figures 7 and 8 in the supplementary material.) Simionescu and Percec recently reported that in these deuterated polymers olefin protons in *E* and *Z* configurations resonate at δ 5.8 and 6.8, respectively,[31] and accordingly, the sharp peaks at δ 5.8 and the apparent absence of peaks at δ 6.8 in the spectra of materials made by using $MoCl_5$, **2**, or **3** imply that the double bonds in these samples almost all have the *E* configuration. In contrast the spectrum of a sample made with WCl_6 looks like that published of a structurally and stereochemically impure polymer.[46]

The infrared spectra (displayed in Figure 8 in the supplementary material) provide support. Those of samples made by using $MoCl_5$, **2**, or **3** exhibit peaks at 890 and 740 cm⁻¹, which have been assigned to units with the *E* configuration.[24,30,45] The spectra are similar to that of poly(pentadeuteriophenylacetylene) that seems to have been made by using ferrous dimethylglyoximate–2pyridine plus $(C_2H_5)_3Al$ as the initiator.[47] In contrast the

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(45) Simionescu, C. I.; Percec, V.; Dumitrescu, S. *J. Polym. Sci.* **1977**, *15*, 2497.

(46) The spectrum resembles spectrum 4 in Figure 2 of ref 31, that of a sample prepared by heating to 140 °C one that was highly cis. But the peak at δ 7.3 (ascribed by Simionescu to polyphenylenic structures) is absent.

Table V. Stereochemistries of Polyalkenamers Obtained by Combining Cycloalkenes C_nH_{2n-2} with Metal Carbyne Initiators $C_6X_5C{\equiv}W(CO)_4Br$ under Vacuum

n	X	[alkene]/ [initiator]	temp, °C	time, h	yield, %[a]	% cis[b] IR	% cis[b] ^{13}C NMR
5	H	255	22	30	7	74	71 ± 3
5	Cl	257	21	15	10	72	72
8	Cl	1000	50[c]	55	6	83	85

[a] As in Table II. [b] As in Table III. [c] The sample was first kept for 13.5 h at 30 °C.

spectrum of polymer made by using WCl_6 as initiator exhibits no apparent absorption at 740 cm^{-1}.

Stereoregularity of the Polyalkenamers. The fraction of the double bonds that are cis in the various polyalkenamers was measured by infrared and ^{13}C NMR spectroscopy.[3a,5,43] For the polynorbornenamer in the first line of Table II whose formation was initiated by the bromometal carbyne **3**, the values are according to the IR analysis 67% cis and according to ^{13}C NMR analysis 80 ± 6% cis. The average is 73.5 ± 6%. This is remarkably similar to the 75.7 ± 5% average measured for samples of polynorbornenamer whose formation was initiated by the Fischer metal carbene **2**.[5] The published values are 75% and 68% cis for two samples and is 84% cis (IR analysis) for another prepared in an unpublished experiment.[48]

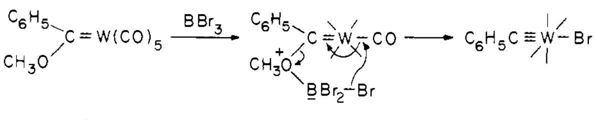
The stereochemistries of many of the polyalkenamer samples prepared here are listed in Tables III and IV. Table V supplements these data with measurements made on samples that are similar to those in Table II. Table VI summarizes the stereochemistries measured for all the samples prepared in this work and compares them with stereochemistries of samples prepared by using related initiators. The comparisons show that the metal carbyne initiator induces fairly high stereoselectivity, somewhat higher than that induced by the combination $WCl_6 + C_6H_5C{\equiv}CH$,[23d] but not as high as that induced by the halogen-free metal carbene of Casey, compound **1**,[3a] or by the combination of the Fischer metal carbene **2** and phenylacetylene.[23b]

The ^{13}C NMR spectra of the cycloalkene polymers discussed here in connection with the polymer stereochemistries also demonstrate that the structures of these materials are those of the polyalkenamers. All of the spectra show only the required peaks and none attributable to impurities, in particular, saturated impurities that would result if double bonds condensed.

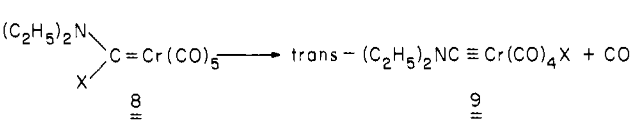
Discussion

The experiments above demonstrate that metal carbenes like **3** initiate polymerizations of acetylenes, and they do this not only with acetylenes that are monosubstituted, but with unsubstituted, disubstituted, and functionalized examples that have rarely or never been polymerized before. The observation is especially remarkable because the ideas presented in the introduction about the mechanism of acetylene metathesis would have metal carbynes inducing acetylenes to metathesize, not polymerize. If the theory about the mechanism of the acetylene polymerization at least is correct, the observation would mean that the metal carbyne is a source of metal carbenes and of ones that are reactive initiators of metathesis reactions.

Although we do not know at this point how the metal carbyne generates metal carbenes (if that is what it is doing), we speculate that a possible way might be by essentially reversing the reaction (eq 3) by which the metal carbyne is prepared.[12,49] Thus, Fischer and Fischer have repeatedly demonstrated that the isolable metal carbenes **8** spontaneously rearrange as in eq 4, examples including those with X = Cl, Br, I, SeC_6H_5, TeC_6H_5, $Sn(C_6H_5)_3$, and $Pb(C_6H_5)_3$.[50] The kinetics of the rearrangements[50b,c,f-h] are in accord with the mechanism of eq 5, and supposing this mechanism to be correct, if step 2 is not too exothermic, the reverse of the reaction might yield coordinatively unsaturated metal carbenes faster than step 1. Transposing these thoughts to metal carbyne **3** suggests that eq 6 might plausibly yield the coordinatively unsaturated metal carbene **10** and might require a smaller free-energy barrier to be surmounted than the 24.5–28.0 kcal/mol required for **1** or **2** to lose CO (eq 7).[51] There is not much evidence supporting this thought, but the similar stereochemistries of the acetylene polymers produced by the initiators **2** and **3**, demonstrated in Figures 2, 3, 4, 7, and 8, accord with the idea, for the initiating species should be **10** and **11** (X = OCH_3), which are similar in structure. The similarities in the stereochemistries of the polynorbornenamers produced by **2** and **3** (Table VI) plausibly reflect this same similarity.

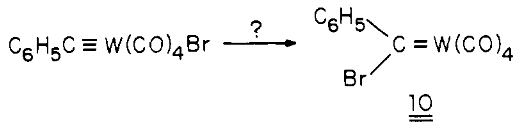


(3)

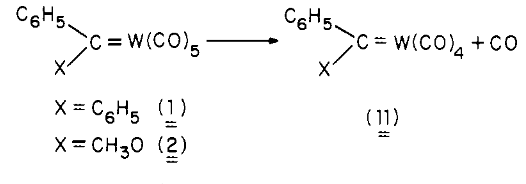


(4)

$$\mathbf{8} \xrightarrow[\text{slow}]{k_1} CO + [(C_2H_5)_2N](X)C{=}Cr(CO)_4 \xrightarrow[\text{fast}]{k_2} \mathbf{9} \qquad (5)$$



(6)



(7)

The observation that the metal carbynes also induce olefins to metathesize and that the cyclopentadienyl-capped metal carbyne **5** induces neither acetylenes nor cyclic olefins to polymerize also agrees with the hypothesis.

The idea also accounts for why Schrock's metal carbyne, **4**, metathesizes acetylenes whereas the Fischer metal carbyne, **3**, polymerizes them, for the Schrock metal carbyne is coordinatively unsaturated while Fischer's is not. If this unsaturation is required for reaction to occur, the Schrock compound can react directly, but the Fischer metal carbyne has to lose a ligand from the metal. If that ligand is the halogen and if it rearranges to the adjacent carbon, the coordinative unsaturation is produced but at the expense of the metal carbyne transforming into a metal carbene.

Whether this hypothesis is correct or not, the essential theoretical point implied by the experiments is that metal carbynes like **3** appear to be sources of metal carbenes.

Experimental Section

The IR spectra in Figures 4 and 8 were recorded by using a Perkin-Elmer Model 1420 spectrometer, and the others by using a JASCO IRA-1. The vapor-phase chromatography (VPC) column was a $^1/_8$ in

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(47) Figure 1, spectrum 3, in ref 31.

(48) The experiment was one of Dr. Nancy Acton's in this laboratory.

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Table VI. Stereochemistries of Polyalkenamers Formed by Various Initiators

cycloalkene	initiator	% cis		ref
		IR	^{13}C NMR	
norbornene	$(C_6H_5)_2C{=}W(CO)_5$	94.5	92.5	*a*
norbornene	$(C_6H_5)(CH_3O)C{=}W(CO)_5$	75.7 ± 5		*b*
norbornene	$C_6H_5C{\equiv}W(CO)_4Br$	73.5 ± 6		*c*
cyclooctene	$(C_6H_5)_2C{=}W(CO)_5$	97	>98	*a*
cyclooctene	$(C_6H_5)(CH_3O)C{=}W(CO)_5 + C_6H_5C{\equiv}CH$	94.3 ± 2	94 ± 1	*d*
cyclooctene	$WCl_6 + C_6H_5C{\equiv}CH$	82.8 ± 3	79.8 ± 5	*e*
cyclooctene	$C_6H_5C{\equiv}W(CO)_4Br$	79.7 ± 4	80.9 ± 5	*c*
cycloheptene	$(C_6H_5)_2C{=}W(CO)_5$	98	98	*a*
cycloheptene	$(C_6H_5)(CH_3O)C{=}W(CO)_5 + C_6H_5C{\equiv}CH$	97 ± 1	96	*d*
cycloheptene	$WCl_6 + C_6H_5C{\equiv}CH$	73.3 ± 0.7	67.9 ± 2	*e*
cycloheptene	$C_6H_5C{\equiv}W(CO)_4Br$	84.3 ± 4	84.3 ± 5	*c*
cyclopentene	$(C_6H_5)_2C{=}W(CO)_5$	91	80	*a*
cyclopentene	$(C_6H_5)(CH_3O)C{=}W(CO)_5 + C_6H_5C{\equiv}CH$	74 ± 8	58	*d*
cyclopentene	$WCl_6 + C_6H_5C{\equiv}CH$	61 ± 2	40 ± 2	*e*
cyclopentene	$C_6H_5C{\equiv}W(CO)_4Br$	69 ± 15	71 ± 10	*c*

[a] Reference 3a. [b] Reference 5. [c] This work. [d] Reference 23b. [e] Reference 23d.

× 9 ft column of 3% Carbowax 20 M on 100–200 mesh acid-washed and dimethylchlorosilylated Chromosorb W or, when specified, a 30 m × 0.316 mm capillary column coated with 0.25-μm Carbowax 20 M. The instrument was a Varian 3700 with flame ionization detector. Gel permeation chromatograms were measured by using tetrahydrofuran (THF) solutions, five μStyragel columns (10^6, 10^5, 10^4, 10^3, and 500 Å) from Waters Associates, and a refractive index monitor.

Preparation and Purification of Monomers. Acetylenes. Phenylacetylene (Aldrich 98%) was distilled through a spinning-band column, and a fraction that was 99.9% pure (VPC analysis) was collected, distilled from CaH_2 at reduced pressure, and stored at −15 °C in a N_2 atmosphere. Propyne (from Matheson Gas Co.) was passed from a lecture bottle through a 31 cm × 3 cm tube packed half with 5-Å molecular sieves and half with 8–14 mesh basic Al_2O_3 from MCB chemicals. *tert*-Butylacetylene (99.6% pure), 2-hexyne, and 5-chloro-1-pentyne (all from Farchan Labs) were distilled through a short column. The latter two were than 99.6% and 99.8% pure (VPC). 2-Butyne was dried over sodium and it and 1-hexyne (Farchan) were distilled through the spinning-band still. Their purities were then 99.9% and 99.7% (VPC). Methyl propiolate (Aldrich 99%) and methyl propargyl ether (Aldrich 98%) were used as received. 5-Cyano-1-pentyne was prepared from 5-chloro-1-pentyne according to the method for the preparation of capronitrile[52] and distilled at 30 mm (bp 85 °C). The yield of materials that were 95–98.5% pure (VPC) was 53%. A fraction that was 98.5% pure was used in the polymerization experiments. ^{13}C NMR 118.5 (CN), 81.4 (C_5), 70.1 (C_6), 24.1 (C_3), 17.3 (C_2), 15.8 (C_4) ppm. Refluxing the 95% pure materials (8.3 g, 89 mmol) and NaOH (700 mmol) in H_2O (400 mL) for 10 h, acidifying with aqueous HCl, extracting with ether, and distilling (110–111 °C (20 mm)) gave a 70% yield of the carboxylic acid. Refluxing (6.5 g, 57 mmol) the carboxylic acid in CH_3OH (60 mL) and 0.2 mL of concentrated H_2SO_4 for 4 h, extracting (ether), washing, drying ($MgSO_4$), and distilling (82–83 °C (43 mm)) gave 5.5 g (76% yield) of the ester. This was redistilled to give 98% pure (VPC) methyl 5-hexynoate.

Pentadeuteriophenylacetylene was prepared from pentadeuterioacetophenone, which itself was prepared according to the literature[53] with some modifications as follows. Acetyl chloride (19.6 g, 0.23 mol) was added during 30 min to a mixture of $AlCl_3$ (33.3 g, 0.25 mol) and C_6D_6 (99% D, 21 g, 0.25 mol) cooled by a cold-water bath (ca. 5 °C). (The mixture suddenly solidified.) After 30 min reflux with 120 mL of *n*-pentane, the solid was broken into small pieces, transferred to a beaker containing 300 g of ice, extracted with 200 mL of pentane, washed (water, aqueous NaOH, water), dried ($MgSO_4$), and distilled through a short column (no rotovap!), finally at ca. 91 °C/23 mm, giving 21 g (67% yield). (The ^{1}H NMR spectrum shows only methyl protons, at δ 2.6). The acetylene was then prepared by the method of Casanova et al.[54] and purified by distillation through a short Vigreaux column (57 °C/35 mm). The overall yield from the acetophenone was 17%. VPC analysis showed the material to be 98.5% phenylacetylene, 0.5% styrene. The only ^{1}H NMR resonance observed was that of the acetylene proton, at δ 2.9.

Cycloalkenes. Cyclopentene (from Aldrich Chemical Co.) was distilled through a spinning-band column and redistilled from CaH_2. The purity (VPC, capillary column) was 99.7%. Cycloheptene (Aldrich, 99.6+% purity) was refluxed with and distilled from Na. Cyclooctene (from Eastman Kodak Co., 96.2%) was partially hydrogenated over 10% Pd/C. The catalyst was filtered, and the hydrocarbon was distilled through a Vigreaux column. It was then refluxed over Na and distilled again. VPC analysis (capillary) showed the material to be 92.7% cyclooctene and 7.3% cyclooctane.

Metal Carbynes. *trans*-Bromotetracarbonyl(phenylmethylidyne)tungsten (**3**) was prepared essentially as described by Fischer et al.[12c] After flash chromatography on silica gel at −25 °C, eluting with pentane–CH_2Cl_2 (6:1), recrystallization from pentane–CH_2Cl_2 at −100 °C, washing with cold pentane, and drying under vacuum at −20 °C for 3 h, the yield of yellow needles was 67%: IR (hexane, ν_{CO}) 2125 (m), 2050 (vs), 1975 (m); lit.[12c] 2125 (m), 2040 cm^{-1} (vs). The ^{13}C NMR spectrum in CD_2Cl_2 at −20 °C exhibited the reported resonances[38] and none that were extraneous.

The chloro and iodo analogues were prepared essentially as described[38] but at somewhat different reaction temperatures. Thus, BCl_3 was added at −5 °C during 15 min and the reaction mixture was then warmed to 5 °C for 30 min. BI_3 in pentane solution was added in 5 min at 0 °C, and the reaction mixture was warmed to 7 °C for 40 min. The metal carbynes were flash chromatographed on silica gel at −25 °C, eluting impurities with pentane–CH_2Cl_2 (5:1) and then the metal carbynes with CH_2Cl_2. They were recrystallized from pentane–CH_2Cl_2 at −100 °C, washed with cold pentane, and dried under vacuum at −20 °C for ca. 5 h. The yields of the chloro and iodo compounds were 59% and 23%, both yellow needles. Their ^{13}C NMR spectra in CD_2Cl_2 at −20 °C exhibited the reported resonances and no extraneous ones.

The cyclopentadienylmetal carbyne **5** was prepared from **3** according to the method of Fischer.[37] The yield was 12%. After purification by flash chromatography on silica gel, eluting with pentane–CH_2Cl_2 (5:1), and recrystallization from pentane (at −78 °C) its ^{1}H NMR spectrum (room temperature, $CDCl_3$, 90 MHz) exhibited peaks at δ 7.35 (5.1 H) and 5.70 (4.9 H) (lit.[37] δ 7.51 and 5.80 in CD_2Cl_2 at −20 °C) and its IR spectrum (thin film, room temperature) at 1995 and 1900 cm^{-1} (lit.[37] 1984, 1905 cm^{-1} in CH_2Cl_2).

trans-Bromotetracarbonyl(pentachlorophenylmethylidyne)tungsten (**7**) was prepared as described previously,[55,56] but the solid (pentachlorophenyl)lithium was not isolated during the preparation of the metal carbene.[56] Thus, the cold (−78 °C) ether solution of this organolithium, prepared from 1.15 g (4.0 mmol) of hexachlorobenzene, was transferred by cannula to a flask containing 1.41 g (4.0 mmol) of $W(CO)_6$ in 500 mL of ether at −70 °C. Before the treatment with $(CH_3)_3O^+BF_4^-$, insoluble material was removed by filtration through a coarse sintered glass frit. The orange-red solid residue remaining when the ether was stripped was flash chromatographed on silica gel, eluting with *n*-pentane. After a colorless forerun, a red fraction gave, after the solvent had been stripped, 0.3 g (12% yield) of red crystals, mp 126–127 °C (lit.[56] yield 29.5%, mp 129 °C). Our IR data match those published. The ^{1}H NMR in $CDCl_3$, δ 3.3, compares with the published δ 3.6.[56] The mass spectrum exhibited the required parent peaks.

This metal carbene (0.18 g, 0.292 mmol) was added under N_2 to a solution of $AlBr_3$ (0.15 g, 0.57 mmol) in CH_2Cl_2 (5 mL, distilled from

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Table VII. ^{13}C NMR Spectra of Poly(5-X-1-pentyne), Where X = Cl, CN, CO_2CH_3

	carbon					
X	1	2	3	4	5	X
Cl[a]	131.7	137.7	31.8	31.8	44.9	
CN[b]	ca. 128.1	137.7	16.7	24.9	16.5	120.2
CO_2CH_3[c]	ca. 129.0	138.5	33.8	24.2	33.8	173.5

[a] Two small extraneous peaks were observed at 37.1 and 29.7 ppm. [b] The assignments of C_3 and C_5 may be reversed. Small extraneous peaks were observed at 32.6 ppm and its vicinity. [c] The methyl resonance is at 51.2 ppm. There were small extraneous peaks in the vicinity of the C_3 and C_5 resonances.

P_2O_5). During 1-h stirring at −78 °C the color changed from orange-red to yellow-green. Solvent was removed at −60 °C by reducing the pressure until 1 ml of solvent remained (ca. 2 h), and CH_3OH (2.5 mL) then precipitated the yellow product. After 10 min at −78 °C, solvent was syringed away, and the residue after three more washings with 2.5 mL of CH_3OH was finally filtered, giving 0.125 g of 7 (67% yield) after drying under a vacuum of ca. 1 mm for 1 h. IR peaks in CH_2Cl_2 were at 2056 (vs) and 2136 (w) cm^{-1}; lit.[55] 2052 (vs), 2137 (w). The molecular weight (mass spectrum) was that required.

All metal carbynes were stored under N_2 at −78 °C.

Polymerization Procedures. Substituted Acetylenes. Propyne (1.3 g, 33 mmol) was condensed, degassed at ca. 10^{-5} mm, and distilled onto the initiator (40 mg) in a 20-mm glass tube. Other acetylenes (ca. 2 mL) were passed through short columns of 80–200 mesh basic Al_2O_3, dehydrated over CaH_2, degassed on the vacuum line, and distilled onto the initiator in 13-mm glass tubes. No solvents were used. The glass tubes were evacuated and sealed. Reactions were effected at room temperature. Polymers were isolated by stirring the contents of the tubes briefly (ca. 20 min) with $CHCl_3$ (ca. 10 mL) and precipitating with methanol (ca. 100 mL). The supernatants were decanted and the polymers dried under vacuum (ca. 0.5 mmHg) for ca. 15 h.

Poly(phenylacetylene) was dark red-orange, soluble in $CHCl_3$, CH_2Cl_2, benzene, and THF. The gel permeation chromatogram showed a long tail at low molecular weights. It was analyzed as though there were one major peak whose characteristics are recorded in Table I and a minor one (whose area on the recording of refractive index was $^1/_8$ as large) with "$\bar{M}_w$" = 45 × 10^3, "$\bar{M}_n$" = 4 × 10^3.

Polypropyne was orange, soluble in $CHCl_3$, CH_2Cl_2, and THF. Its infrared spectrum appears below in the supplementary material. Its ^1H NMR spectrum in $CDCl_3$ (80 MHz) is like that published: δ 5.9 (broad) and 1.7, with much smaller peaks at 0.9, 2.2, and 2.6.

Poly(*tert*-butylacetylene) was a white powder, soluble in THF and $CHCl_3$. Its ^{13}C NMR spectrum was like that published, with olefin resonances at 144.6 (C_1) and 128.1 (C_1) ppm (C_2) and methyl resonances exhibited in Figure 4: IR (thin film) 2960–2880 (=CH, CH_3), 1600 (weak and broad, C=C), 1480, 1460 (sh), 1390, 1360, 1240, 1200 cm^{-1} (in agreement with a spectrum displayed by Masuda et al.[16a] for a sample prepared by using WCl_6 in CCl_4 as the initiator, although in their spectrum peaks at 1200 and 1240 cm^{-1} were not resolved). Poly(1-hexyne) was a red-orange polymer, soluble in $CHCl_3$ and THF: IR (thin film) 1620 (broad and weak) and prominently 2840–2960 (CH), 1460, 1380, 1100, 930, 900 cm^{-1}; ^1H NMR (in $CDCl_3$, 80 MHz) δ 5.8 (0.8 H, H_1), 2.2 (2.0 H, H_2), 1.3 (4.1 H, H_4), 0.9 ppm (3.1 H, H_5).

Poly(2-hexyne) was a white powder, soluble in benzene, THF, $CHCl_3$, and CH_2Cl_2. Its ^{13}C NMR, ^1H NMR, and IR spectra match those published:[26] ^1H NMR ($CDCl_3$ at 300 MHz) δ 2.1 (H_1), 1.7 (H_4), 1.4 (H_5), and 0.9 (H_6) ppm; ^{13}C NMR 138.0 (C_3), 131.9 (C_2), 36.7 (C_4), 21.4 (C_5,C_1), 14.7 (C_6) ppm; IR (thin film) 1650 (very weak, C=C), 2940 (s), 2880 (s), 2935 (sh), 1470 (m), 1455 (m), 1380 (m), 1105 (m), 1060 (sh), 1000 (w) cm^{-1}; $[\eta]_{sp}$ = 2.34 ± 0.04 in toluene at 30.1 °C.

Poly(2-butyne) was a white powder, partially soluble in $CHCl_3$. Its ^1H NMR spectrum in $CDCl_3$ (80 MHz), like that published, exhibits the CH_3 resonance at δ 1.6 ppm and no olefin resonance.

The polymers of 5-chloro- and 5-cyano-1-pentyne are orange; that of methyl 5-hexynoate is reddish brown. All are soluble in THF and $CHCl_3$. Their ^{13}C NMR spectra, displayed in Figure 1 and in the supplementary material, exhibit the peaks summarized in Table VII. The IR spectrum of poly(5-cyano-1-pentyne) as a thin film has peaks at 2940 (s), 2880 (m), 2250 (s, CN), 1690 (w), 1455 (m), and 1425 cm^{-1} (m). The ^1H NMR spectrum of the polymer at 200 MHz consists of three peaks: δ 5.92 (0.72 H), 2.40 (3.89 H), and 2.40 (2.40 H). These IR and ^1H NMR spectra are displayed in the supplementary material.

Attempt To Polymerize Methyl 5-Hexynoate with 2. The ester (1.4 g, 11.1 mmol), which had been passed through basic alumina, was degassed and distilled from CaH_2 onto **2** (40 mg, 0.090 mmol) contained in an evacuated glass tube. The tube was then sealed. After 4 days at 45 °C no polymer was obtained.

Acetylene. Metal carbyne **3** (33.5 mg, 0.072 mmol) was placed in a 250-mL round-bottomed flask containing a Teflon stirring bar and connected by a fused length of 8-mm o.d. glass tubing to a vacuum manifold. The flask was evacuated to a pressure of 1.5 × 10^{-5} mmHg. This flask and the other glassware used in the experiment had been dried in an oven at 110 °C for at least 10 h. *m*-Xylene (5 mL), which had passed through a short column of basic alumina directly into a 25-mL flask containing a small amount of CaH_2, was degassed on the manifold in three freeze–thaw cycles and transferred through the manifold to the flask containing **3**. This flask was then evacuated again and cooled in liquid N_2.

Meanwhile, acetylene, obtained from Matheson Gas Co. in acetone solution, was purified by passing it through a train, initially evacuated, consisting of these components: a trap cooled in dry ice/acetone, an H_2SO_4-filled trap, an empty trap, a column of KOH, a column of crushed basic alumina, and a column of 5-Å molecular sieves. The acetylene stream was allowed to flow through the vacuum manifold system while the flask containing the initiator and solvent was isolated and cooled. One gram of the gas was measured into the reaction vessel by noting the pressure drop in the sealed manifold when the reaction flask was opened to the system. Residual acetylene was evacuated. The flask was evacuated again at −194 °C and then sealed with a torch.

The reaction took place while the flask was stirred at room temperature for 92 h. The flask was then broken open in a glove bag under N_2, and the black polymer coating the walls was scraped off, washed with distilled *n*-pentane, and filtered through a coarse ground glass frit in a Schlenk tube. After drying under vacuum for 24 h, the yield was measured as 339 mg (34% yield). The elemental analysis (C, 85.93; H, 7.16; O, 3.66) showed carbon and hydrogen atoms to be present in the ratio 1.007 and small amounts of oxygen-containing impurities to be present too. (The ratio of oxygens and carbons was 0.03.) Figure 6 displays the ^{13}C NMR spectrum of this sample.

Cycloalkenes. (a) Under Vacuum. Each cycloalkene was passed through a column of basic alumina. Then a sample of ca. 1.5 g over CaH_2 was degassed by three freeze–thaw cycles under a vacuum of <10^{-5} mm and distilled under vacuum onto the initiator contained in a glass tube. The tube was melted shut and stored at room temperature. The polymer was isolated by dissolving the reaction mixture in $CHCl_3$, precipitating with methanol, decanting the solvent, and drying under vacuum (ca. 0.5 mm) for 12 h.

(b) In the Atmosphere. The cycloalkenes were passed through alumina and ca. 1.5-g samples were simply combined with the initiator in a flask that was then sealed with a serum bottle cap.

(c) Under N_2. Reactions were effected in small flasks that were repeatedly evacuated and filled with N_2. In the example with metal carbyne **6** and cyclopentene a volume of CH_2Cl_2, freshly distilled from P_2O_5, was present equal to that of the cyclopentene. Otherwise no solvents were used.

(d) In the Presence of Oxygen. Metal carbyne **3** (40 mg, 0.086 mmol) was placed in a glass tube whose volume (3.3 mL) when sealed by a Teflon valve was the sum of the required volume of cycloalkene and oxygen. This tube was connected by ground glass joints to another containing cyclopentene (1.3 mL, 1.0 g, 14.7 mmol) over CaH_2, and both tubes were connected to a source of high vacuum. The cyclopentene was degassed and distilled onto the metal carbyne, oxygen (0.082 mmol) was allowed to fill the apparatus, and the Teflon valve was closed. The experiments with cycloheptene and cyclooctene were similar.

(e) In the Presence of H_2O. The required amount of water was added to cyclopentene, and a weighed portion was degassed and distilled onto the initiator.

Norbornene. A solution of norbornene (1.5 g, Aldrich 99%, refluxed with and distilled from Na just before) in toluene (0.5 mL, previously washed with H_2SO_4, NaOH, dried with $CaCl_2$, and distilled from Na) was degassed and distilled onto the initiator. The contents of the sealed reaction tube which solidified 5 min after warming to room temperature were stirred with 6 mL of CH_2Cl_2 for ca. 20 min and poured into ca. 15 mL of CH_3OH.

Solubilities of the Polymers. Polypent-, -hept-, and -octenamers were completely soluble in $CHCl_3$, tetrahydrofuran, benzene, and CH_2Cl_2. Polyhept- and -octenamers dissolved in $CHCl_3$ quickly (ca. 20 min) while polypentenamer dissolved slowly (3 h). Polynorbornenamer was only partially soluble in $CHCl_3$.

Attempts To Use 5 as an Initiator. Phenylacetylene (0.93 g, 9.1 mmol) that was distilled through a spinning-band column and redistilled from CaH_2 (99.4% pure, 0.6% styrene, according to VPC analysis) was passed through a column of 80–200 mesh basic alumina, dried over CaH_2, degassed, and distilled onto the initiator (20 mg, 0.043 mmol) contained in an evacuated glass tube. The tube was sealed and after 3 days at room temperature was cracked open. Pouring into methanol (10 mL), cen-

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trifuging, washing with methanol, and drying (vacuum, 24 h) gave only 1.5 mg (1.6% yield) of orange powder.

Norbornene (0.75 g, 8.0 mmol, the sample used above, freshly distilled) in toluene (1 mL, the same as above, just passed through a short column of basic alumina) was dried and degassed over CaH_2 in three freeze–thaw cycles under high vacuum. After distillation onto the initiator (14.0 mg, 0.030 mmol) and sealing under vacuum, the mixture was warmed to room temperature. The color turned from orange to brown in 3 days. Pouring into ca. 10 mL of methanol gave no precipitate.

Effect of O_2 On Polymerization of Cyclopentene by 1. Cyclopentene (1.4 mL, 14.6 mmol, refluxed over CaH_2 and distilled just before) was passed through a column of basic alumina. By use of the apparatus described above in the experiment with **3** and O_2, it was dried and degassed over CaH_2 (three freeze–thaw cycles under high vacuum) and distilled onto **1** (48 mg, 0.098 mmol). Oxygen (0.1 mmol) was admitted, and the tube was then warmed at 43–45 °C. After ca. 1 h the original purple color had faded. After ca. 24 h the reaction mixture was still not noticeably viscous. Pouring into ca. 10 mL of CH_3OH at this point precipitated no polymer.

The same experiment was conducted simultaneously without oxygen. (The evacuated tube was simply sealed after the cyclopentene had been distilled onto the initiator.) The reaction mixture solidified in 3 h and after 24 h was dissolved in ca. 3 mL of $CHCl_3$ and precipitated with CH_3OH. After drying under vacuum for 12 h, the yield was 0.835 g (84%).

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Registry No. 3, 50726-27-7; **7**, 62342-88-5; poly(phenylacetylene), 25038-69-1; polypropyne, 28391-48-2; poly(*tert*-butylacetylene), 51730-68-8; poly(1-hexyne), 28827-85-2; poly(2-pentyne), 28904-75-8; poly(2-butyne), 25684-85-9; polyacetylene, 25067-58-7; poly(5-chloro-1-pentyne), 88996-53-6; poly(methyl 5-hexynoate), 88996-54-7; poly(5-cyano-1-pentyne), 88996-55-8; poly(methyl propargyl ether), 57884-03-4; poly(methyl propiolate), 27342-21-8; polynorbornene, 25038-76-0; polycyclopentene, 25103-85-9; polycyclooctene, 25267-51-0; polycycloheptene, 26426-65-3; $C_6H_5C{\equiv}W(CO)_4Cl$, 50726-26-6; $C_6H_5C{\equiv}W(CO)_4I$, 50726-28-8; polypentenamer, 28702-43-4; polyoctenamer, 28702-45-6; polyheptenamer, 28702-44-5; polynorbornenamer, 42813-64-9.

Supplementary Material Available: ^1H NMR spectrum of poly(*tert*-butylacetylene) prepared in experiment 4 of Table I, ^{13}C NMR spectrum of poly(acetylene) (experiment 9 in Table I), ^1H NMR and IR spectra of 4 samples of poly(pentadeuteriophenylacetylene), IR spectrum of poly(propyne) prepared in experiment 3, Table I, ^{13}C NMR spectra of poly(methyl 5-hexynoate) and poly(5-chloro-1-pentyne) prepared in experiments 10 and 11 in Table I, and ^1H NMR and IR spectra of poly(5-cyano-1-pentyne), prepared by repeating experiment 12 in Table I on a larger scale (11 pages). Ordering information is given on any current masthead page.

Stereocontrolled Synthesis of Trans-2,5-Disubstituted Tetrahydrofurans

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Abstract: A process is described for the stereospecific construction of trans-2,5-disubstituted tetrahydrofurans, involving 2,4,4,6-tetrabromo-2,5-cyclohexadienone-induced cyclization of γ,δ-unsaturated alcohols to the 3-bromotetrahydropyrans followed by ring contraction. Control over the side-chain stereochemistry can also be exerted, as exemplified by the sequence **6** → **7** → **8**. To probe the possibility that 1,3 relative asymmetric induction manifested by this strategy could prevail over an opposing 1,2 influence, construction of a model of the 2,3,5-trisubstituted tetrahydrofuran ring of ionophores such as monensin was investigated. In this instance, highly polarized olefins, such as (trimethylsilyl)methyl-substituted alkenes or methyl enol ethers, were required for Markovnikov orientation. Although the desired 2,3-cis-2,5-trans substitution pattern could be introduced, the cyclization reaction was not stereospecific in these instances.

The synthesis of polyether antibiotics remains a challenge, requiring methods for the stereocontrolled construction of oxacyclic rather than carbocyclic rings.[1] The 2,5-disubstituted tetrahydrofuran units, which are common to these natural products, are particularly troublesome since 1,3-interactions are weak in five-membered rings. Although electrophilic cyclization of γ,δ-unsaturated alcohols is one of the most direct routes to such systems,[2] these cyclizations generally proceed with only modest stereoselectivity.[3] As an example, 2-methyl-6-octen-3-ol (Z:E mixture, 1:3) is cyclized with 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCO)[4] to give a 56:44 ratio of trans/cis tetrahydrofurans (71% yield); iodine (I_2, Na_2CO_3, acetonitrile) is only slightly more selective, giving a 75:25 ratio of trans/cis isomers (48% yield). We sought therefore a procedure for specific generation of the trans isomers, not only to overcome the limitations of direct cyclization but also as a complement to our previously reported strategy for the selective formation of cis-2,5-disubstituted tetrahydrofurans.[3b]

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