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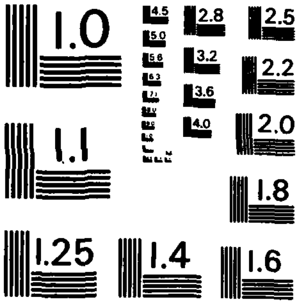

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Trans-[bromotetracarbonyl(phenylmethylidyne)tungsten] and related metal-carbynes induce acetylenes and cycloalkenes to polymerize. The acetylenes include examples that are monosubstituted, disubstituted, and unsubstituted, as well as the first reported 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

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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.

OFFICE OF NAVAL RESEARCH

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TECHNICAL REPORT NO. 5

Polymerizations of Acetylenes and Cyclic Olefins Induced by Metal-Carbynes

by

Thomas J. Katz, Thoi Huu Ho,
Neng-Yang Shih, Yuan-Chi Ying,
and Van I.W. Stuart

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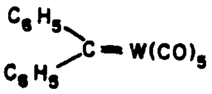
Introduction

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, Casey's pentacarbonyl(diphenylmethylene)tungsten[2] (1) initiating metatheses 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-*t*-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.

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 equation 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 (regretably in this case giving, as do all other effective initiators, only insoluble polymers),[14a,15,19,20] and



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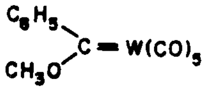

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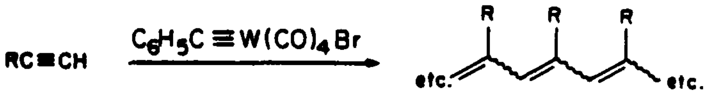
$C_6H_5C \equiv W(CO)_4Br$

3

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

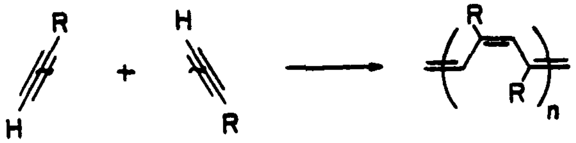
4



(1)

acetylenes with functional groups remote from the triple bond.[21] (Polymers of these last materials had not previously been prepared.)

If we suppose that the acetylene polymerization is an olefin metathesis[17,23,24] ---that is, that it involves the formal transformation summarized in equation 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 induce their substrates to give products that are identical, in particular in stereochemistry. Experiments testing these notions are also described.



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Results

Polymerizations of Acetylenes. Table 1 summarizes experiments testing how effective metal-carbyne $\underline{3}$ 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 ($\underline{1}$ and $\underline{2}$).[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 $\underline{1}$.[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 $\underline{2}$.) The ^1H NMR spectrum of poly(1-hexyne)[17] and the ^1H and ^{13}C NMR spectra of poly(2-hexyne)[26] and poly(t-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 polyphenylacetylene formed using the metal-carbyne 3 as the initiator (see figure 3b below) resembles one reported recently by Simionescu and Percec for a sample prepared using the initiator Co(acetylacetonate)$_3$ plus $(C_2H_5)_3Al$.[29a] 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 below 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 1), 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 1, 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 below, 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 1. After 4 days at 45 °C no polymer whatever was obtained.

The new polymers have been characterized by their ^{13}C NMR spectra, which are summarized in Table 7 in the Experimental Section. 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 ^{1}H 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 below 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 1 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.

$C_6H_5C \equiv W(CO)_2(\eta^5-C_5H_5)$ $\qquad$ $CH_3C \equiv W(CO)_4Br$

5 $\qquad$ 6

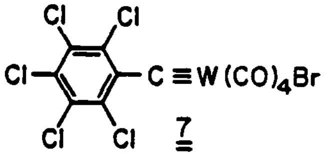
Other halocarbynes related to 3, however, do initiate the polymerizations, the methylbromocarbyne 6,[38] for example, inducing propyne to polymerize. (When combined with 333 equivalents of the acetylene for 11 days at -15 °C ---the methylcarbyne is notably unstable--- this metal-carbyne gave an 11% yield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

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

Polymerizations 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 polymerizes 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 co-catalysts have been studied.

Table 2 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



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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 is combined with the cyclopentadienyl-capped metal-carbyne 5 under the same conditions used in experiment 1 in Table 2, no polymer was isolable even after 3 days.

The other cyclic olefins in Table 2 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 can not 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 to 9 times as much as the unsubstituted metal-carbyne. Experiments described below using the metal-carbyne 6 also accord with this trend, for under reaction conditions similar to those in the table, this thermally less stable metal-carbyne[38] is seen to be a bad initiator for cyclopentene's polymerization.

Table 3, 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 co-catalyze 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 one mole of oxygen per mole of metal-carbene 1 is present, the yield of polypentenamer obtained when cyclopentene is incubated with 1/150 mole of 1 for 24 h at 44 °C falls to zero 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 halo-metal-carbyne with chlorine[38] does not. (Replacement with iodine,[38] however, decreases the yields from the less active alkenes.) Table 4 summarizes relevant data. This replacement of bromine by chlorine is also without effect if the reactions are performed in a 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 mole) polymerized cyclopentene to an extent of 5% (71% *cis* according to IR or ^{13}C NMR analysis), whereas 3 itself (1/172 mole) 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 2 carbon monoxides) is replaced by a cyclopentadienyl unit, giving 5, this material, just as in the experiment with norbornene described above, has no measureable initiating ability in similar experiments. For example under conditions like those in Table 4, after 96 h cycloheptene (74 moles) in the atmosphere gave no polymer, and neither did cyclopentene (170 moles).

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(t-butylacetylene). Figure 2 compares the methyl ^{13}C nuclear magnetic resonances and the olefin ^{1}H nuclear magnetic resonances (a full spectrum is in figure 5 in the supplementary material) of samples of poly(*t*-butylacetylene) that had been prepared 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 and b imply that 82.3 ± 1% of the double bonds in both polymers have the *E* configuration. The ^{1}H 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 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 ^{13}C resonances is correct, the low field proton resonance is associated with *E* olefin units.

Stereoregularity of Polyphenylacetylene. The ^1H NMR and infrared spectra of samples of polyphenylacetylene prepared using 3 as the initiator are compared in figures 3 and 4 with the spectra of samples prepared 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 using bromocarbyne (3), and 75 ± 10% for polymer made using Fischer carbene (2). The sample made using WCl_6 exhibited no peak at δ 5.8 ppm, and accordingly the double bonds are < 13 ± 10% *cis*. The ^1H NMR and infrared spectra of samples of poly(pentadeuteriophenyl-acetylene) prepared 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 ppm respectively,[31] and accordingly the sharp peaks at δ 5.8 and the apparent absence of peaks at 6.8 ppm in the spectra of materials made 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 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(pentadeuteriophenyl-acetylene) that seems to have been made using ferrous dimethylglyoximate·2-pyridine plus $(C_2H_5)_3Al$ as the initiator.[47] In contrast the spectrum of polymer made 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 2, whose formation was initiated by the bromo-metal-carbyne 3, the values are: according to the IR analysis 67% *cis*; and accordingly 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 [illegible] 75% and 68% *cis* for two samples, and was 84% *cis* (IR analysis) for another [illegible] prepared in an unpublished experiment.[48]

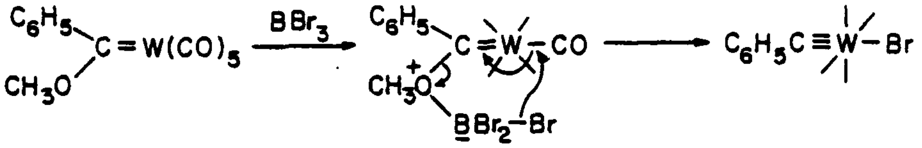
The stereochemistries of many of the polyalkenamer samples p[illegible]d here are listed in Tables 3 and 4. Table 5 supplements these data with measurements made on samples that are similar to those in Table 2. Table 6 summarizes the stereochemistries measured for all the samples prepared in this work and compares them with stereochemistries of samples prepared 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

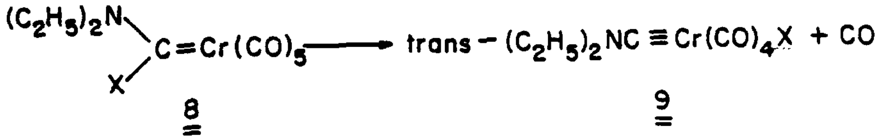
The experiments above demonstrate that metal-carbenes like 3 initiate polymerizations of acetylenes, and they do this not only with acetylenes that are monosubstituted, but with unsubstituted, disubstituted, and functionalized examples that have rarely or never been polymerized before. The observation 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 (equation 3) by which the metal-carbyne is prepared.[12,49] Thus Fischer and Fischer have repeatedly demonstrated



(3)

that the isolable metal-carbenes 8 spontaneously rearrange as in equation 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,g,h] are in accord with the mechanism of equation 5, and supposing this mechanism to be correct, if

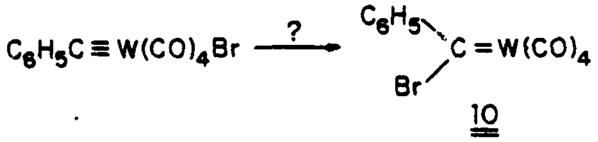


(4)

step 2 is not too exothermic, the reverse of the reaction might yield coordina-

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

tively unsaturated metal-carbenes faster than step 1. Transposing these thoughts to metal-carbyne 3 suggests that equation 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/mole required for 1 or 2 to



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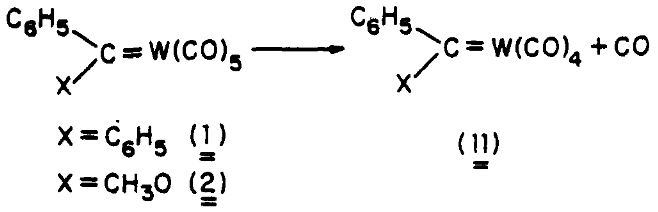

(7)

lose CO (equation 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 6) plausibly reflect this same similarity.

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 Figure 4 and 8 were recorded using a Perkin-Elmer model 1420 spectrometer, and the others using a JASCO IRA-1. The vapor phase chromatography (VPC) column was a 1/8" x 9' column of 3% carbowax 20 M on 100-200 mesh acid-washed and dimethylchlorosilylated chromosorb W or, when specified, a 30 m x 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 using tetrahydrofuran (THF) solutions, five μ-styragel 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 x 3 cm tube packed half with a Å molecular sieves and half with 8-14 mesh basic Al_2O_3 from MCB chemicals. Tertiary-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 then 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 Hg (bp 85 °C). The yield of materials that was 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 at 20 mm Hg) 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 concd H_2SO_4 for 4 h extracting (ether), washing, drying ($MgSO_4$) and distilling (82-83 °C, 43 mm Hg) 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 *n*-pentane, the solid was broken into small pieces, transferred to a beaker containing 300 g ice, extracted with 200 mL pentane, washed (water, aqueous NaOH, water), dried ($MgSO_4$), distilled through a short column (no rotovap!), finally at *ca.* 91°/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 in a vacuum at -20 °C for 3 h, the yield of yellow needles was 67%. IR (hexane, ν_{CO}) 2125(m), 2050(vs), 1975(m); reported[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 in a 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 cyclopentadienyl metal-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 ^1H NMR spectrum (room temperature, $CDCl_3$, 90 MHz) exhibited peaks at δ 7.35 (5.1 H) and 5.70 ppm (4.9 H) (literature[37] 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} (literature[37] 1984, 1905 cm^{-1}, in CH_2Cl_2).

Trans-[bromotetracarbonyl(pentachlorophenylmethylidyne)tungsten], 7, was prepared as described previously,[55,56] but the solid pentachlorophenyllithium 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) $W(CO)_6$ in 500 mL 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 that 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 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 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 CH_3OH was finally filtered, giving 0.125 g 7 (67% yield) after drying in a vacuum of ca. 1 mm Hg for 1 h. IR peaks in CH_2Cl_2 were at 2056(vs) and 2136(w) cm^{-1}; reported:[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 in a vacuum (ca. 0.5 mm Hg) for ca. 15 h.

Polyphenylacetylene 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 1 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 ^{1}H 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 ppm.

Poly(*t*-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 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.*[10a] for a sample prepared 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 in $CDCl_3$ 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). $[\eta]_{spc} = 2.34 \pm 0.04$ 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 7. 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 ppm (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} mm Hg. This flask and the other glassware used in the experiment had been dried in an oven at 110 °C for at least 10 h. Meta-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; 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 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, and the black polymer coating the walls was scrapped off, washed with distilled n-pentane, and filtered through a coarse ground glass frit in a Schlenk tube. After drying in a 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) In a 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 in a vacuum of $< 10^{-5}$ mm and distilled in the 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 in a 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 CH_2Cl_2 for ca. 20 min and poured into ca. 15 mL CH_3OH.

Solubilities of the Polymers. Polypent-, hept-, and oct-enamers were completely soluble in $CHCl_3$, tetrahydrofuran, benzene, and CH_2Cl_2. Polyhept- and oct-enamers 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), centrifuging, 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 in a high vacuum. After distillation onto the initiator (14.0 mg, 0.030 mmol) and sealing in a vacuum, the mixture was warmed to room temperature. The color turned from orange to brown in 3 days. Pouring into *ca.* 10 mL 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. Using the apparatus described above in the experiment with **3** and O_2, it was dried and degassed over CaH_2 (three freeze-thaw cycles in a 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 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 $CHCl_3$ and precipitated with CH_3OH. After drying in a vacuum for 12 h, the yield was 0.835 g (84%).

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

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

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Figure Captions

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 1.

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

Figure 3. ^{1}H NMR spectra of polyphenylacetylenes (in $CDCl_3$, at 300 MHz for b and c, and at 200 MHz for a and d). (a) Polymer made using $MoCl_5$ (references 16c and 24) in benzene (ca. 22 °C, 2 h), monomer concentration ([M])=2.2 M, initiator concentration ([I])=$4.4\text{x}10^{-2}$ M; (b) Polymer made using bromocarbyne 3 as initiator (Table 1, Sample 1); (c) Polymer made using Fischer carbene (2) as initiator (reference 17), no solvent, [M]/[I]=125, 50 °C, 3 h; (d) Polymer made using Casey's metal-carbene (1) as initiator, no solvent, [M]/[I]=100, 50 °C, 4 h; (e) polymer made using WCl_6 (references 16c and 24) as initiator and CH_2Cl_2 as solvent (ca. 22 °C, 2½ h), [M]=0.9M, [I]=0.9x10M.

Figure 4. Infrared spectra of polyphenylacetylene 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. The samples were prepared as described in the caption to figure 5 using (a) $MoCl_5$, (b) 3, (c) 2, (d) 1, (e) WCl_6.

Figure 1

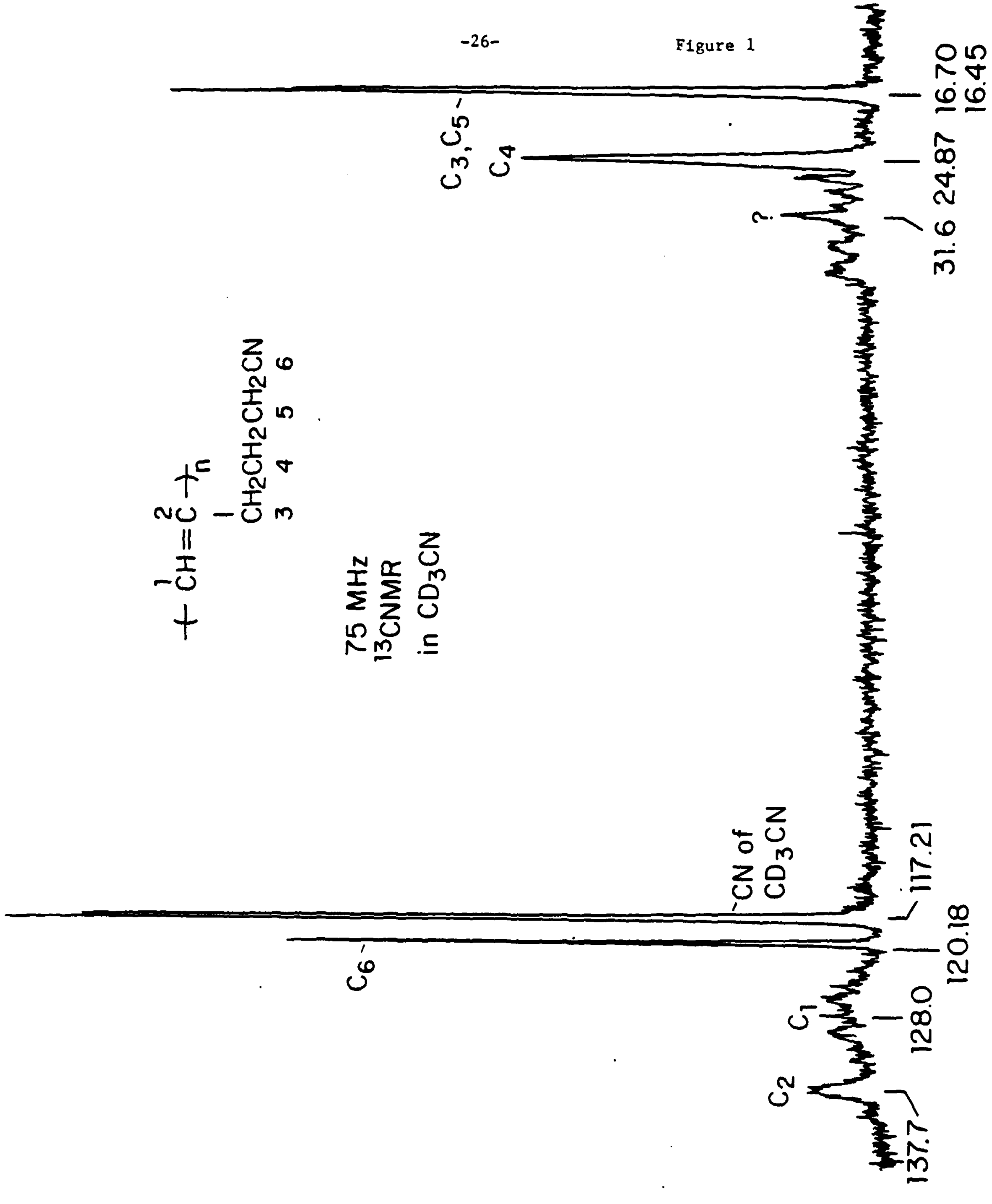
$-(\overset{1}{C}H=\overset{2}{C}-)_n$
$CH_2CH_2CH_2CH_2CN$
3 4 5 6
75 MHz
$^{13}CNMR$
in CD_3CN
C_3, C_5
C_4
?
16.70
16.45
24.87
31.6
CN of CD_3CN
117.21
120.18
C_6
C_1
128.0
C_2
137.7

Figure 2

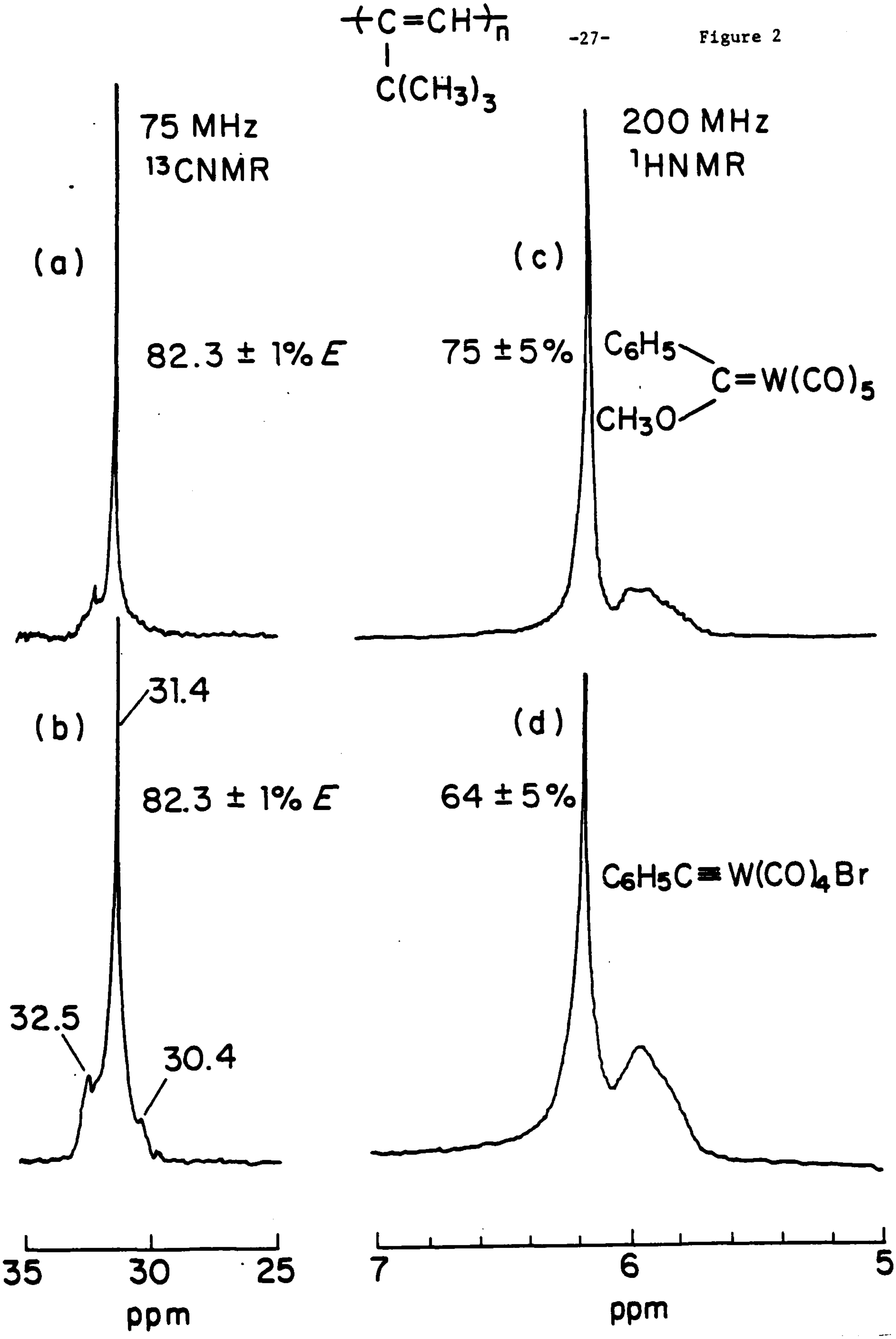
$+C=CH+_n$
$C(CH_3)_3$
75 MHz
^{13}CNMR
200 MHz
^{1}HNMR
(a)
82.3 ± 1% E
(c)
75 ± 5%
C_6H_5
$C=W(CO)_5$
CH_3O
(b)
31.4
82.3 ± 1% E
32.5
30.4
(d)
64 ± 5%
$C_6H_5C\equiv W(CO)_4Br$
35
30
25
ppm
7
6
5
ppm

Figure 3

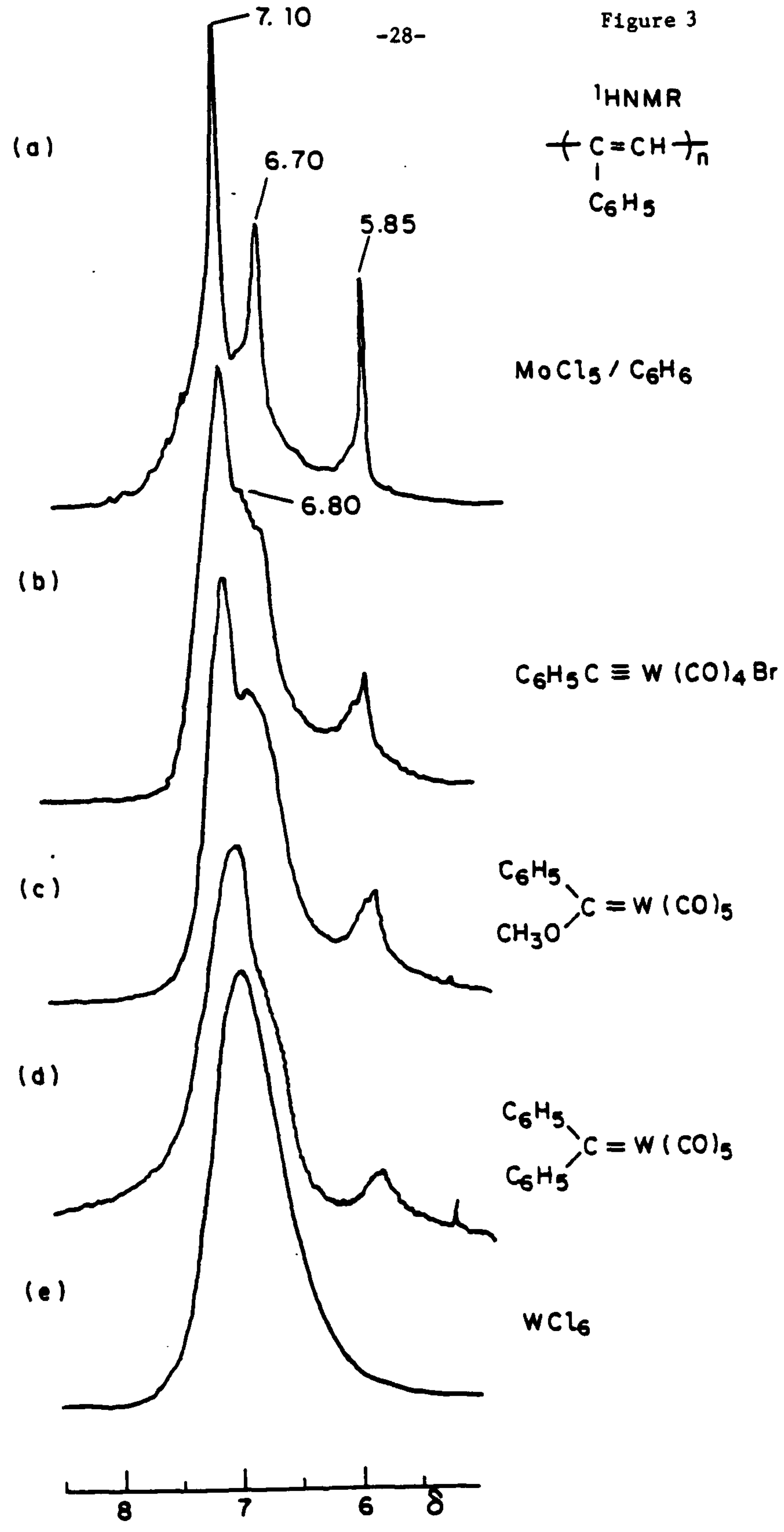
7.10
¹HNMR
$-\!\!(\underset{\underset{C_6H_5}{|}}{C}=CH)\!\!-_n$
(a)
6.70
5.85
MoCl$_5$ / C$_6$H$_6$
6.80
(b)
C$_6$H$_5$C ≡ W (CO)$_4$Br
(c)
C$_6$H$_5$ / CH$_3$O C = W (CO)$_5$
(d)
C$_6$H$_5$ / C$_6$H$_5$ C = W (CO)$_5$
(e)
WCl$_6$
8
7
6
δ

Figure 4

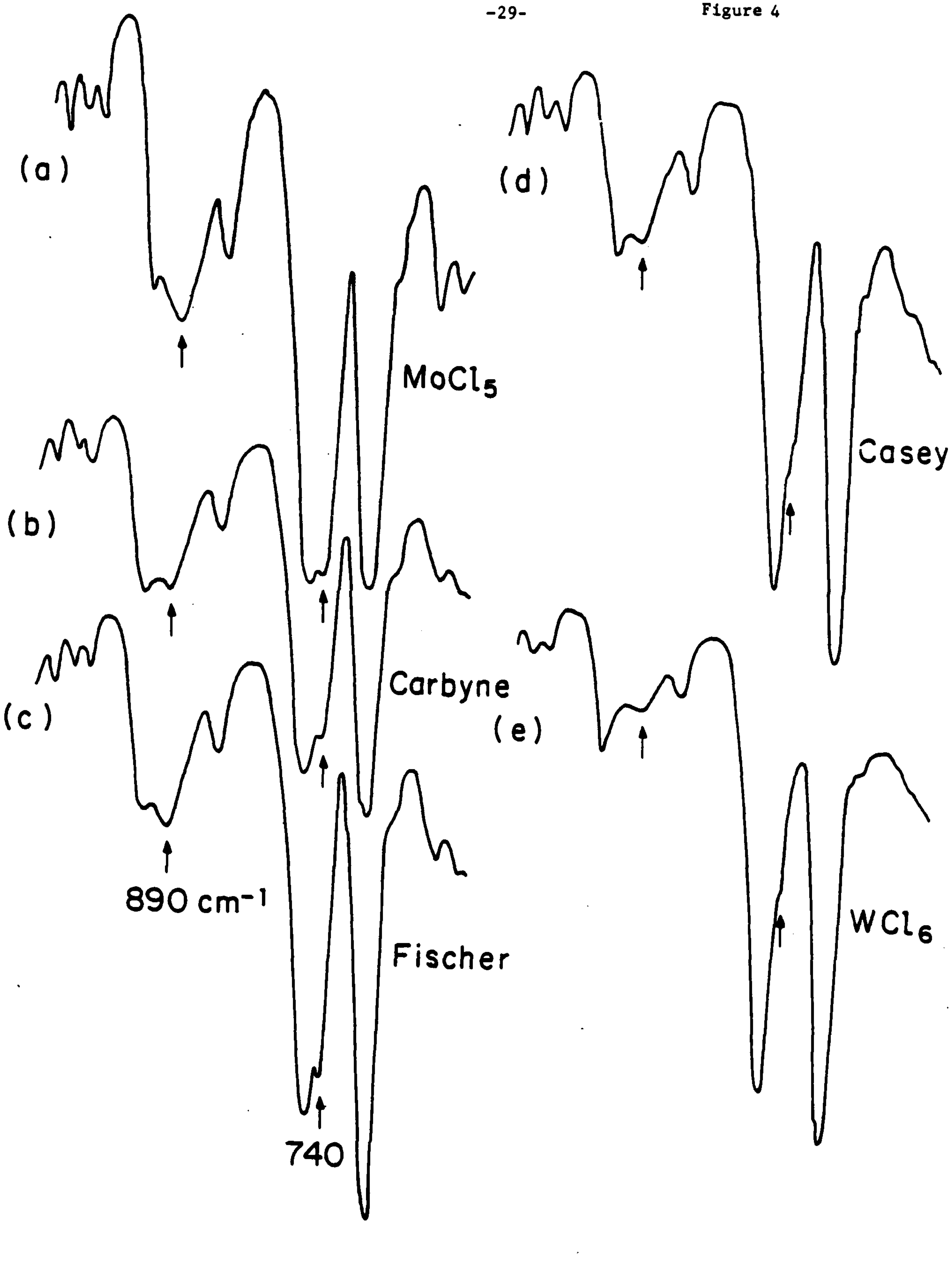

Table 1. Yields and Molecular Weights of Polyacetylenes Obtained by Combining Various Acetylenes with the Initiator $C_6H_5C{\equiv}W(CO)_4Br$ at Ambient Temperature (ca. 22 °C)[a]

Expt. No.	Acetylene	[Acetylene]/[Initiator]	Time (h)	Yield (%)[b]	"$\bar{M}_w$" x 10^{-3}[c]	"$\bar{M}_n$" x 10^{-3}[c]	$\bar{M}_w/\bar{M}_n$
1	$C_6H_5C{\equiv}CH$	212	3	10	151	55	2.8
2	$C_6H_5C{\equiv}CH$	210	14	63	-	-	-
3	$CH_3C{\equiv}CH$	380	8	52	14.4	5.9	2.4
4	$(CH_3)_3CC{\equiv}CH$	190	3	26	-	-	-
5	$(CH_3)_3CC{\equiv}CH$	190	48	39	180	70.1	2.6
6	n-$C_4H_9C{\equiv}CH$	200	48	64	120	49.0	2.4
7	$CH_3C{\equiv}CC_2H_5$	209	20	20	296	174	1.7
8	$CH_3C{\equiv}CCH_3$	350	19	12[d]	-	-	-
9	$HC{\equiv}CH$	536	92	34	-	-	-
10	$HC{\equiv}C(CH_2)_3Cl$	218	2.5	53	201	67	3.0
11	$HC{\equiv}C(CH_2)_3CO_2CH_3$	147	38	16	14.0	5.8	2.4
12	$HC{\equiv}C(CH_2)_3CN$	80	48	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	5	-[f]	-	-

[a] Reactions were effected in evacuated sealed glass tubes. No solvent was used except in the polymerization of acetylene, where 5 mL xylene was present per gram of acetylene. [b] After stirring with $CHCl_3$, precipitating with CH_3OH, and drying in a vacuum. [c] Measured by gel-permeation chromatography using tetrahydrofuran solutions, a refractive index monitor, and 5 Waters Associates μ-styragel 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 $CHCl_3$.

Table 2. Yields and Molecular Weights of Polyalkenamers Obtained by Combining Cyclic Alkenes with Metal-Carbyne Initiators [$C_6X_5C{\equiv}W(CO)_4Br$] in a Vacuum

Alkene	X	$\frac{[\text{Alkene}]}{[\text{Initiator}]}$	Temperature (°C)	Time (h)	Yield (%)[a]	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$[b]
Norbornene	H	267	22	0.08	40[c]		
Cyclopentene	H	172	22	72	5.7		
"	Cl	1000	40	24	20	283	133
Cyclooctene	H	178	22	144	0.8		
"	Cl	250	40	103	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 in a vacuum. [b] Measured by Gel Permeation chromatography as in Table 1. The weights recorded are one half the weights of polystyrenes that would exhibit chromatograms like those observed (see reference 23c). [c] Only partially soluble in $CHCl_3$ or CH_2Cl_2.

Table 3. Yields and Molecular Weights of Polyalkenamers Obtained by Combining Cyclic Alkenes C_nH_{2n-2} with $RC \equiv W(CO)_4Br$ Under Various Conditions in a High Vacuum ("V"), in Air ("A"), after Addition of 1 Mole O_2 ("O") or 1 Mole of Water ("W") per Mole of Metal-Carbyne to the Thoroughly Evacuated Reaction Mixture, or in Flasks Superficially Flushed with Nitrogen ("N").[a] Also Listed are Molecular Weights and the Fraction of the Double Bonds that are cis

								%cis	
n	R	Condition	$\frac{[\text{Alkene}]}{[\text{Metal-Carbyne}]}$	Time (h)	Yield (%)[b]	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$[c]	IR[d]	^{13}C NMR[e]
8	C_6H_5	V	73	24	0.5				
"	"	A	"	"	38	240	138	81	78
"	"	N	"	60	12			92	79 ± 1
"	"	O	"	24	16				
7	"	V	83	24	1				
"	"	A	"	"	50	350	195	84	85 ± 4
"	"	C	"	"	26			89	
5	"	V	172	72	5.7				
"	"	O	"	24	82	313	184	69	59 ± 2
"	"	W	"	144	6				
"	"	N	200	1	35	261	365		
"	"	A	256	30	43	370	210	71	65 ± 4
"	CH_3	V	250	213	0.3				
"	"	N	226	108	2			90	89

[a] 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 2. [d] Measured by infrared spectroscopy as described in reference 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 references 3a,5,43). The errors listed are the average deviations of these measurements.

Table 4. Yields of Polyalkenamers Obtained by Combining Cyclic Alkenes C_nH_{2n-2} with Different Halo-tungstentetracarbonyl(phenylalkylidynes), $C_6H_5C{\equiv}W(CO)_4X$, in the Atmosphere at Ambient Temperature. Stereochemistries and Molecular Weights are also Presented.[a]

Alkene	X	$\frac{[\text{Alkene}]}{[\text{Metal-Carbyne}]}$	Time (h)	Yield (%)[b]	% cis IR[c]	% cis ^{13}C NMR[d]
Cyclooctene	Cl	66	20	36	75	74 ± 2
"	Br	73	24	38	81	78
"	I	79	96	5		85 ± 0
Cycloheptene	Cl	74	20	35	80	81 ± 1
"	Br	81	24	50	84	82 ± 4
"	I	87	96	5		90 ± 1
Cyclopentene	Cl	163	20	77	73	70 ± 7
"	Br	256	30	43	71	65 ± 4
"	I	150	20	60		64 ± 4

[a] The three samples with X=Br are the same as the ones in Table 3. Their molecular weights are listed in that table. [b] After precipitation from $CHCl_3$ with CH_3OH and drying in a vacuum. [c] See Table 3, note d. [d] See Table 3, note e.

Table 5. Stereochemistries of Polyalkenamers Obtained by Combining Cycloalkenes C_nH_{2n-2} with Metal-Carbyne Initiators $C_6X_5C{\equiv}W(CO)_4Br$ in a Vacuum

n	X	[Alkene] / [Initiator]	Temp-ature (°C)	Time (h)	Yield (%)[a]	% cis[b]	
						IR	^{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 2. [b] As in Table 3. [c] The sample was first kept for 13.5 h at 30 °C.

Table 6. Stereochemistries of Polyalkenamers Formed by Various Initiators

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

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

Table 7. ^{13}C NMR Spectra of Poly(5-X-1-pentyne), where X = Cl, CN, CO_2CH_3

X	Carbon					
	1	2	3	4	5	X
Cl[2]	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.

Supplementary Material

Polymerizations of Acetylenes and Cyclic Olefins Induced by Metal-Carbynes

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Figure 5. ^{1}H NMR spectrum of poly(t-butylacetylene) (sample 4 in Table 1) in $CDCl_3$. The resonance frequency is 200 MHz and 260 scans are averaged. Chemical shifts are displayed below the peaks and intensities above.

Figure 6. ^{13}C NMR spectrum of solid polyacetylene (experiment 9 in Table 1). The spin rate is 2655 revolutions per second, the cross polarization time 1 msec, and the number of scans averaged is 63,464. The peaks marked ssb are spinning side-bands. The peaks around 22 and 44 ppm are caused by impurities.

Figure 7. ^{1}H NMR spectra of polypentadeuteriophenylacetylenes (in $CDCl_3$, at 200 MHz, 20 °C). (a) polymer made using as the initiator $MoCl_5$, in benzene (ca. 22 °C, 2½ h), monomer concentration ([M])=10 M, initiator concentration ([I])=0.2 M; (b) polymer made using as the initiator bromocarbyne 3, no solvent, [M]/[I]=100 (ca. 22 °C, 6 h); (c) polymer made using as the intiator Fischer carbene as an initiator, no solvent, [M]/[I]=100, 50 °C, 6½ h; (d) polymer made using as the initiator WCl_6 in CH_2Cl_2 (ca. 22 °C, 2½ h), [M]=10 M, [I]=0.2 M.

Figure 8. IR spectra of polypentadeuteriophenylacetylene. The arrows indicate the positions of the peaks at 890 and 740 cm^{-1} that are supposed to be characteristic of the E configuration. The polymers were prepared as described in the caption to figure 7 using as initiators (a) 3, (b) $MoCl_5$, (c) 2, and (d) WCl_6.

Figure 9. IR spectrum of a film of poly(propyne) prepared in experiment 3, Table 1.

Figure 10. ^{13}C NMR spectrum (75 MHz, 6000 scans) of poly(methyl 5-hexynoate), prepared in experiment 11 in Table 1, in $CDCl_3$.

Figure 11. ^{13}C NMR spectrum (75 MHz, 5600 scans) of poly(5-chloro-1-pentyne), prepared in experiment 10 in Table 1, in $CDCl_3$.

Figure 12. ^{1}H NMR spectrum (200 MHz, 176 scans) of poly(5-cyano-1-pentyne), prepared by repeating experiment 12 in Table 1 on a larger scale, in CD_3CN.

Figure 13. IR spectrum of poly(5-cyano-1-pentyne) as a thin film. The sample is the same as the one used for figure 1.

Figure 5

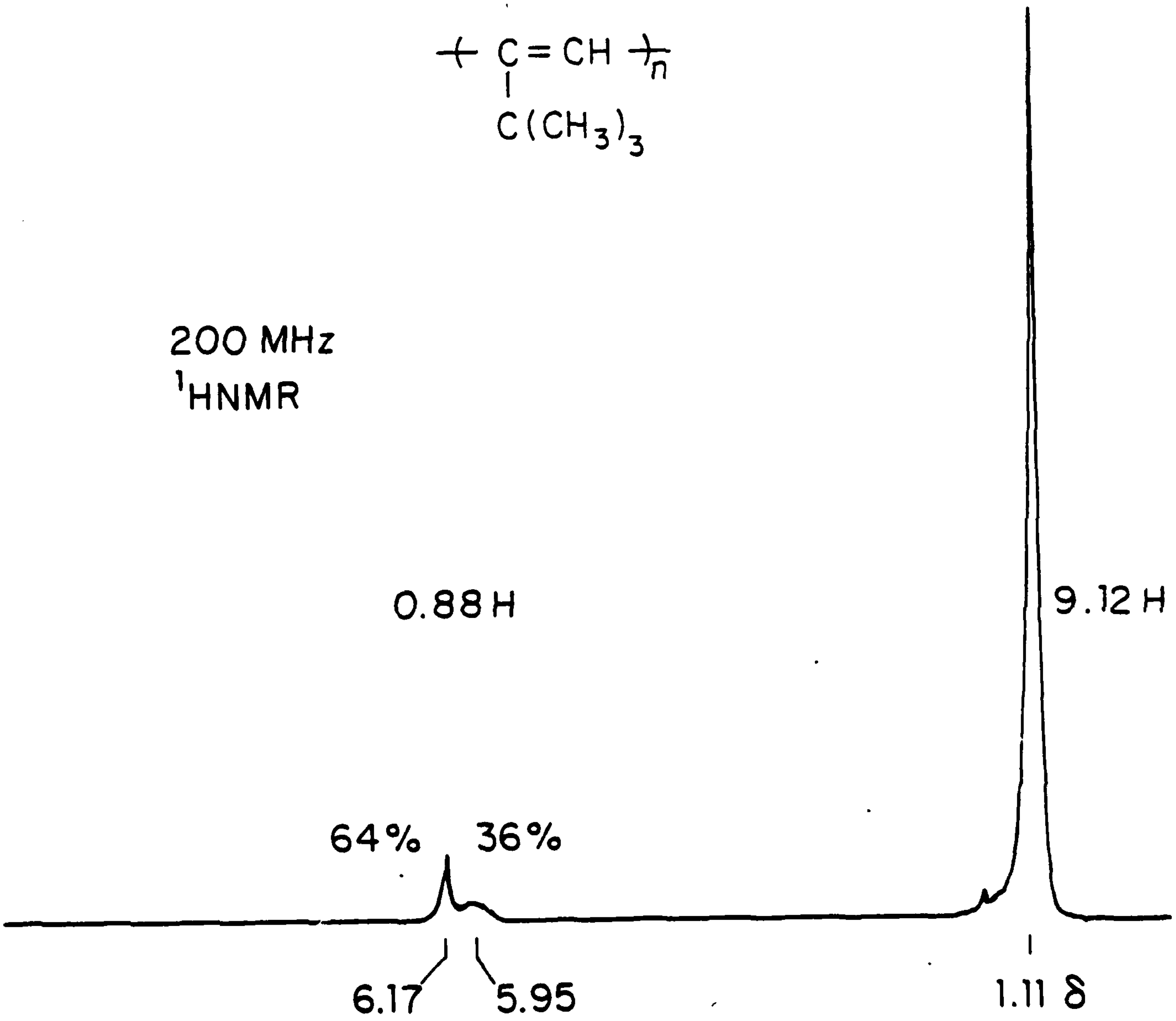


Figure 6

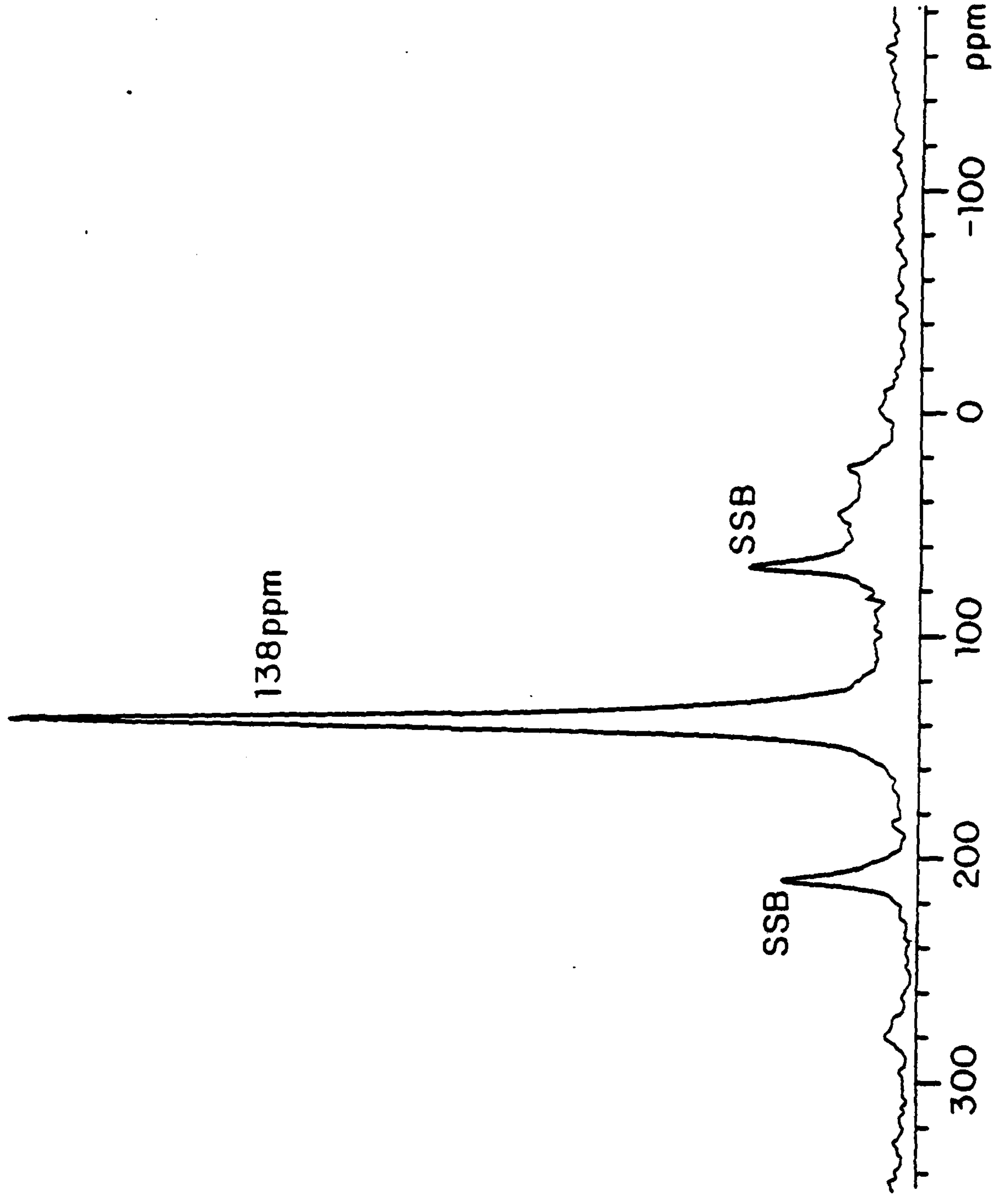


Figure 7

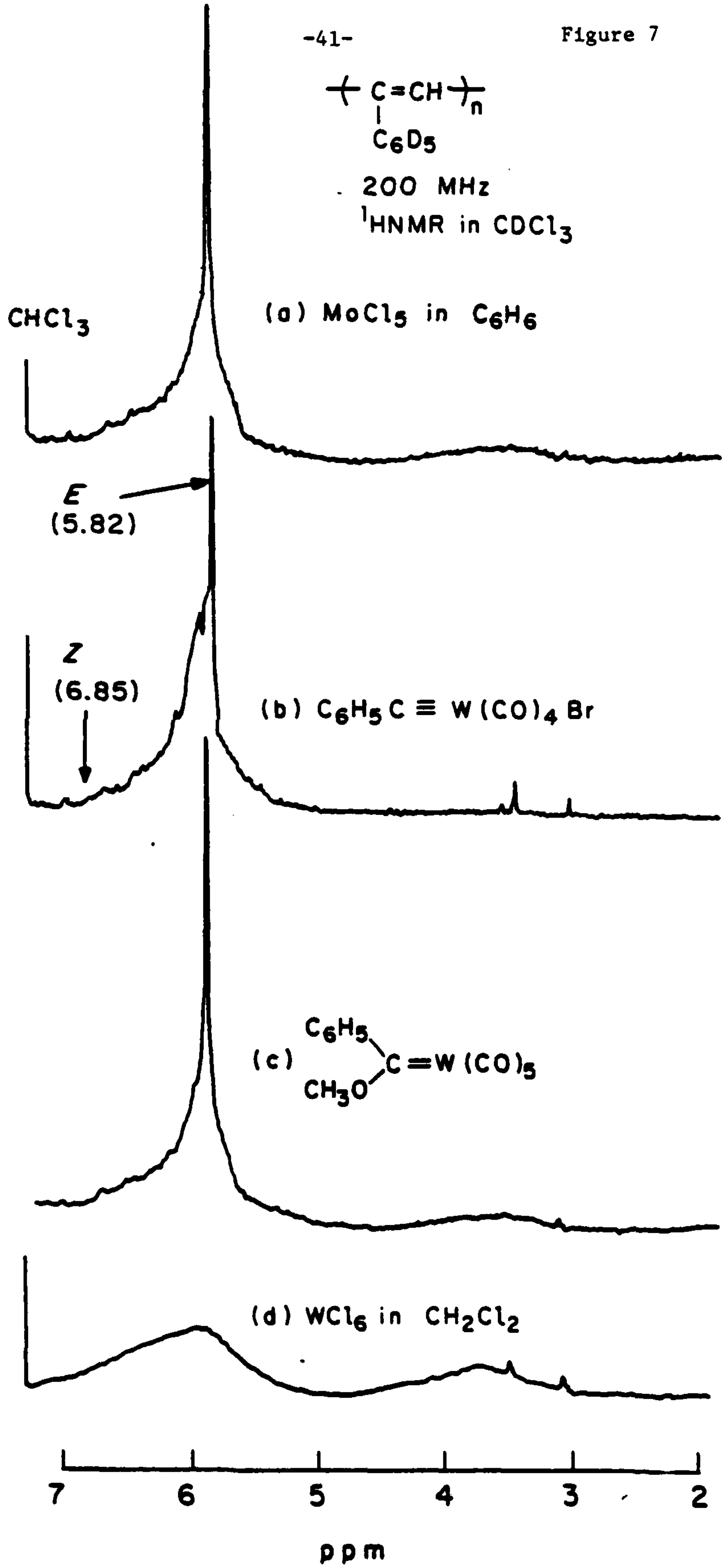

$-\!\!\!\left(\, \underset{\displaystyle C_6D_5}{\underset{|}{C}}=CH \,\right)\!\!\!-_n$
200 MHz
^{1}HNMR in $CDCl_3$
$CHCl_3$
(a) $MoCl_5$ in C_6H_6
E
(5.82)
Z
(6.85)
(b) $C_6H_5C \equiv W(CO)_4Br$
(c) C_6H_5 / CH_3O $C=W(CO)_5$
(d) WCl_6 in CH_2Cl_2
7
6
5
4
3
2
ppm

Figure 8

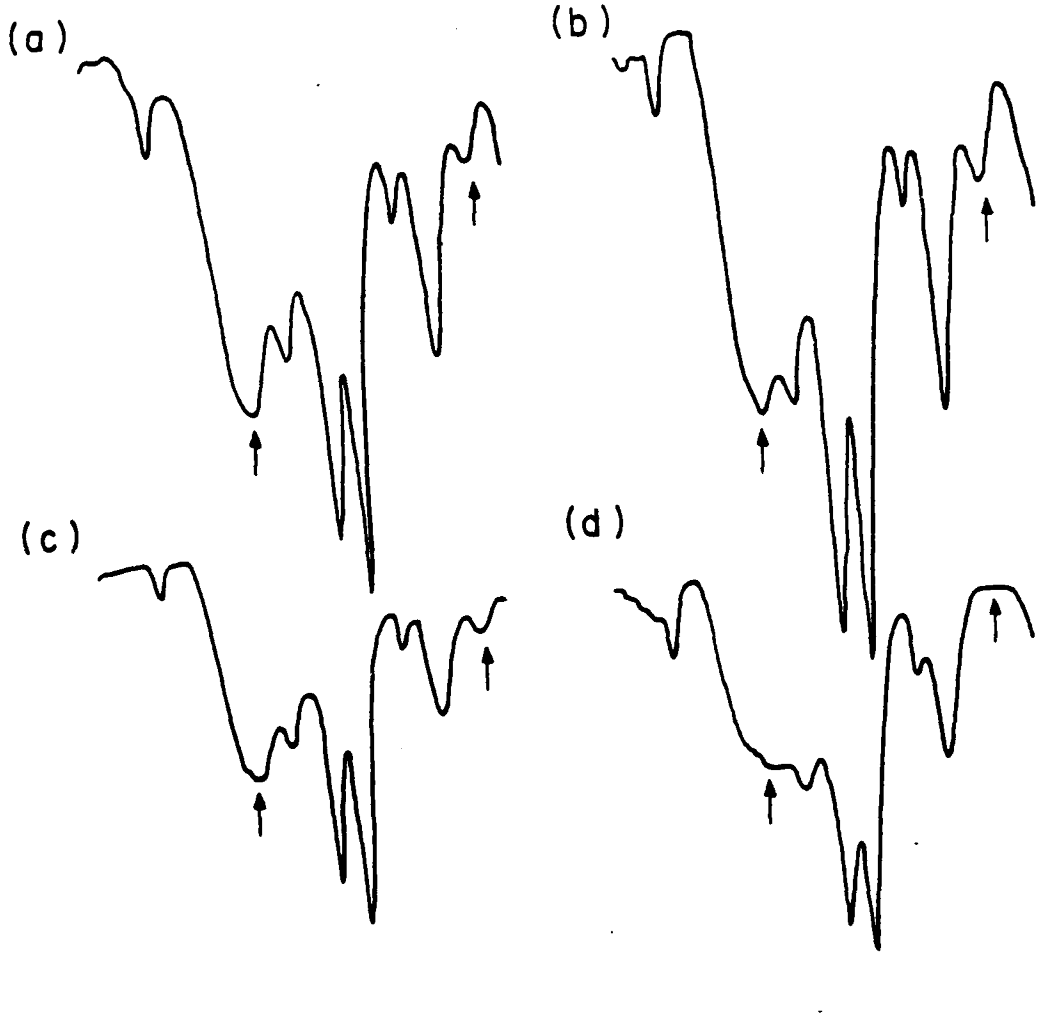
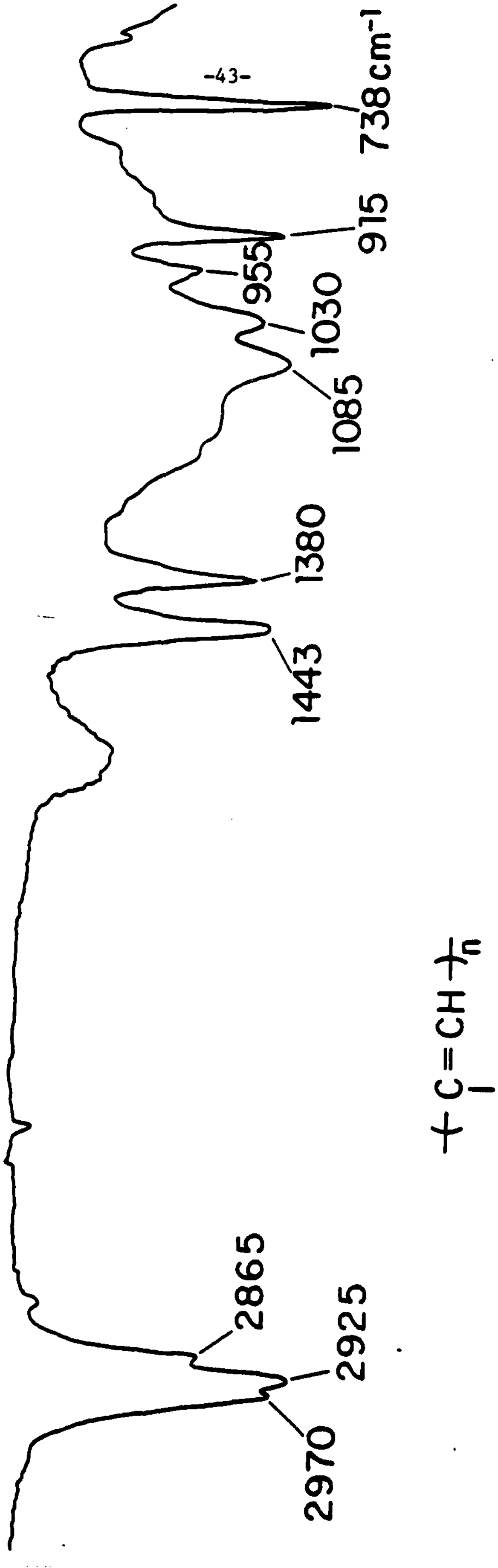


Figure 9


738 cm⁻¹
915
955
1030
1085
1380
1443
2865
2925
2970
$-\!\!\left(\underset{\mathrm{CH_3}}{\mathrm{C}}=\mathrm{CH}\right)\!\!-_n$

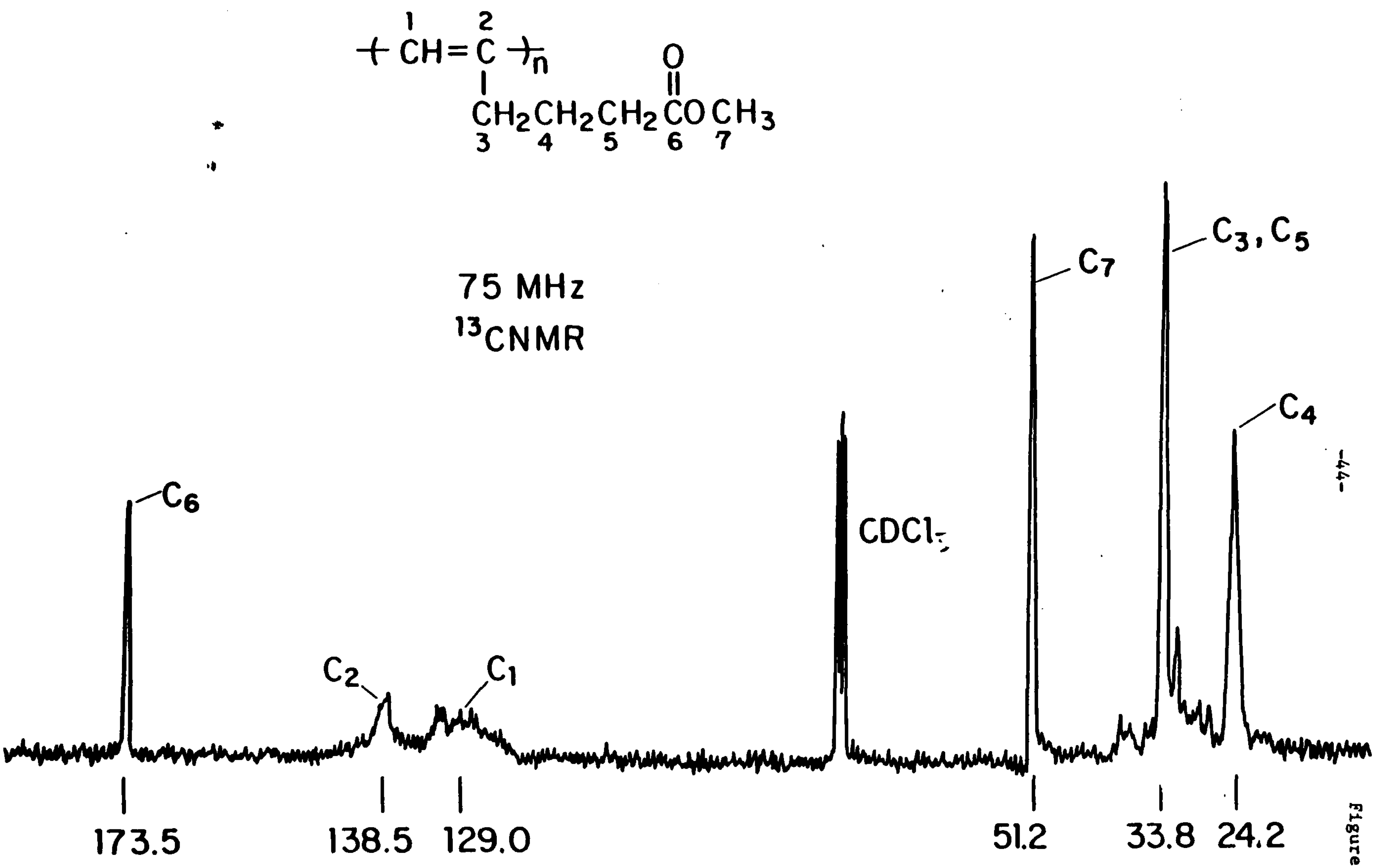

75 MHz
^{13}CNMR
1
2
$\leftarrow CH=C \rightarrow_n$
O
$CH_2CH_2CH_2COCH_3$
3
4
5
6
7
C6
C2
C1
CDCl3
C7
C3, C5
C4
173.5
138.5
129.0
51.2
33.8
24.2

Figure 10

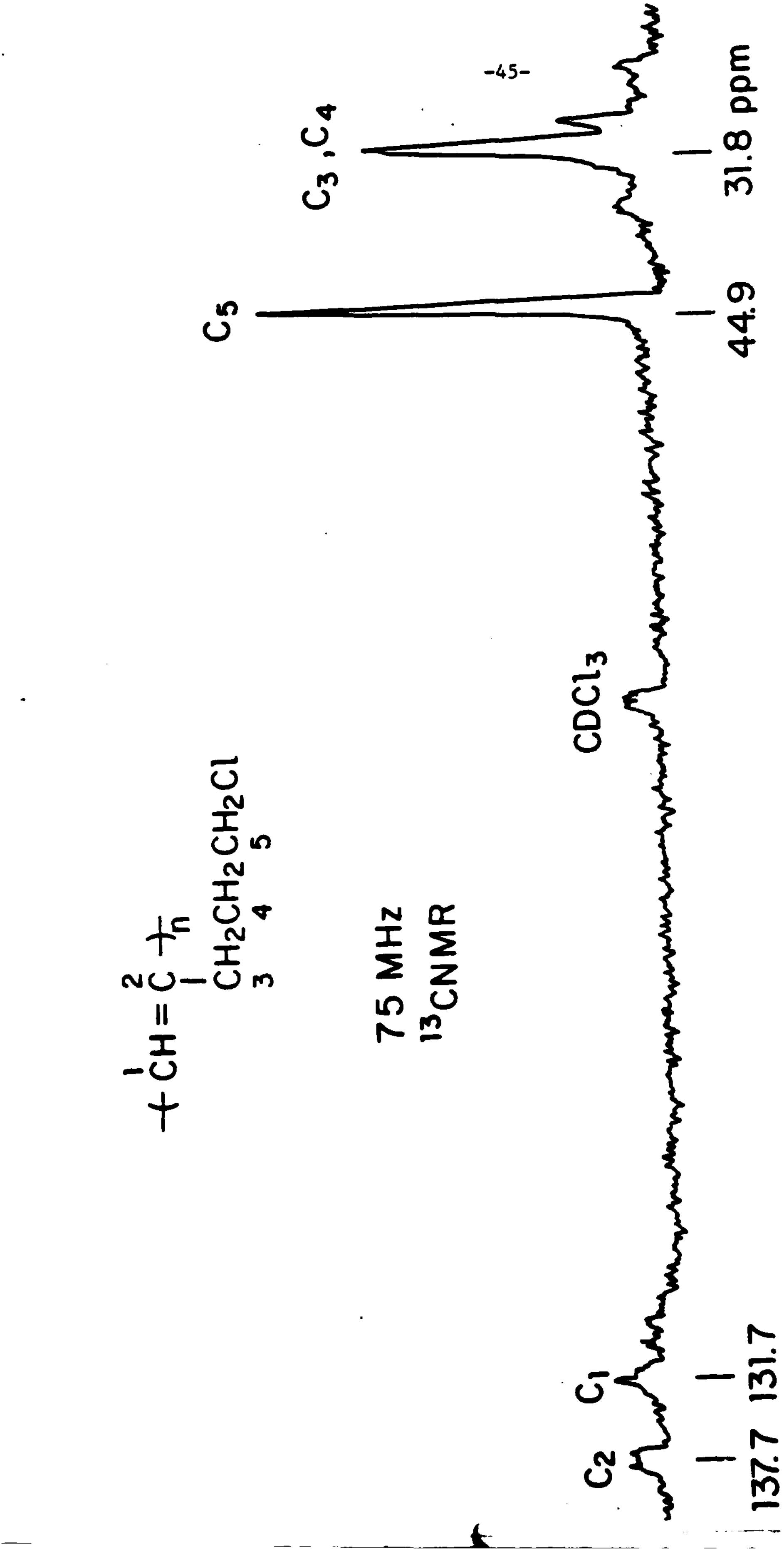

$+\overset{1}{C}H=\overset{2}{C}+_n$
$\overset{|}{\underset{3}{CH_2}}\underset{4}{CH_2}\underset{5}{CH_2}Cl$
75 MHz
^{13}CNMR
C_2
C_1
CDCl$_3$
C_5
C_3, C_4
137.7
131.7
44.9
31.8 ppm

Figure 11

Figure 12

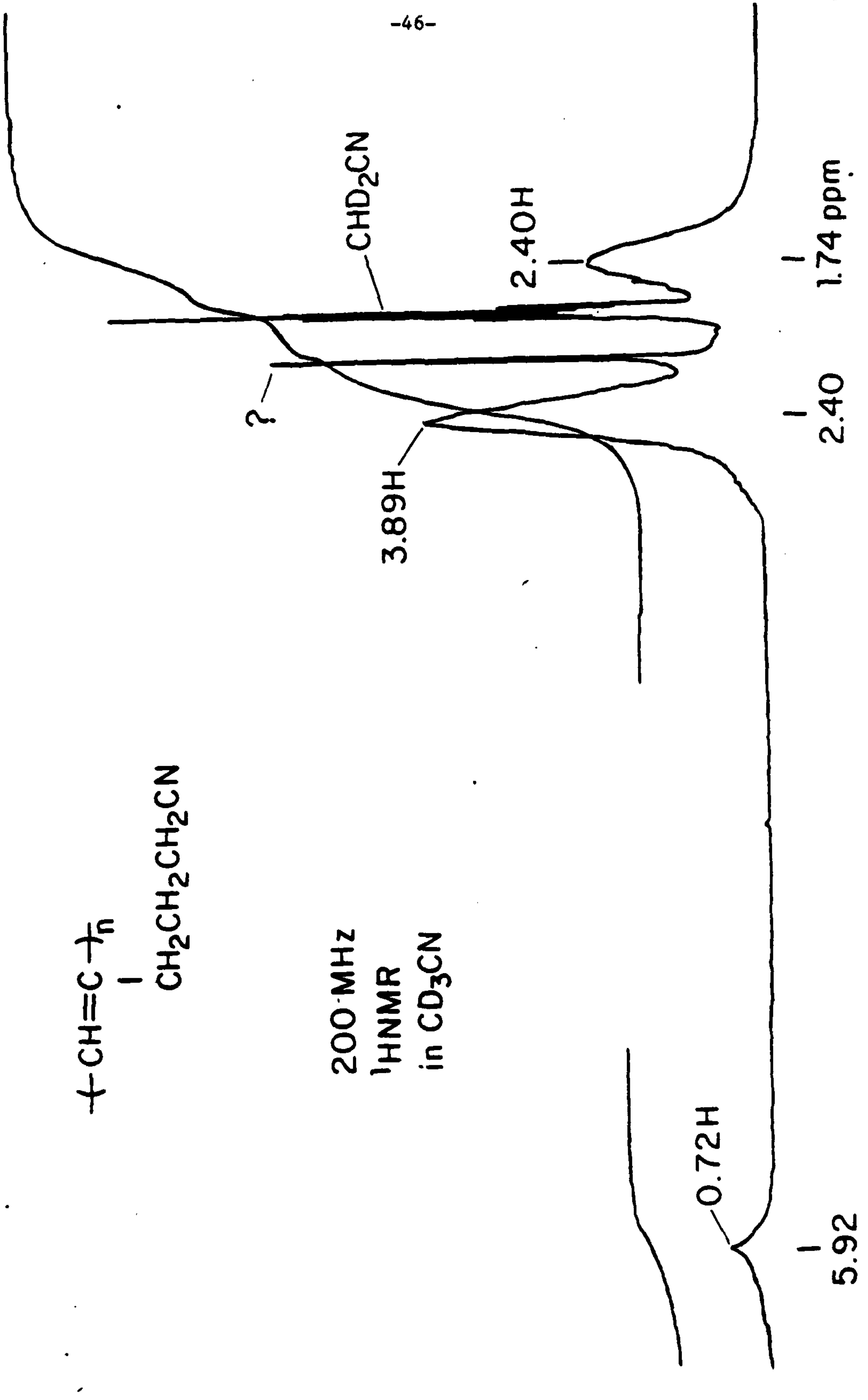
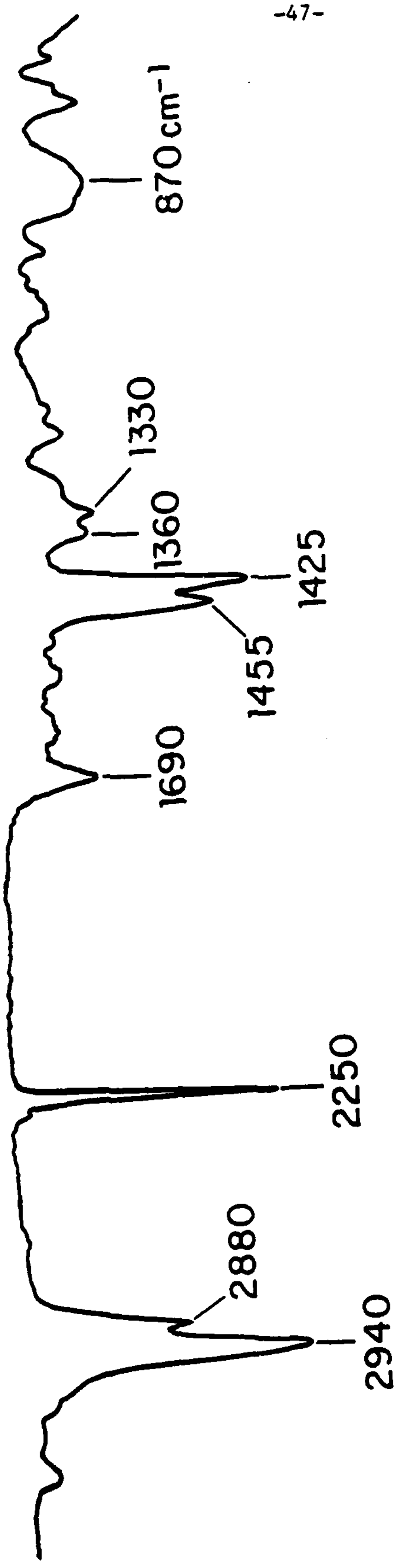
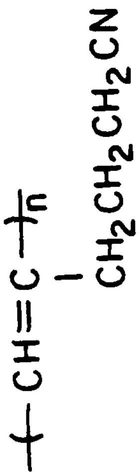

$-\!\!\left(CH{=}C\right)\!\!-_n$
$CH_2CH_2CH_2CN$
200 MHz
^{1}HNMR
in CD_3CN
CHD_2CN
2.40H
?
3.89H
0.72H
1.74 ppm
2.40
5.92

Figure 13





$-\!\!\left[\mathrm{CH{=}C}\right]\!\!-_n$ with $CH_2CH_2CH_2CN$ on C

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