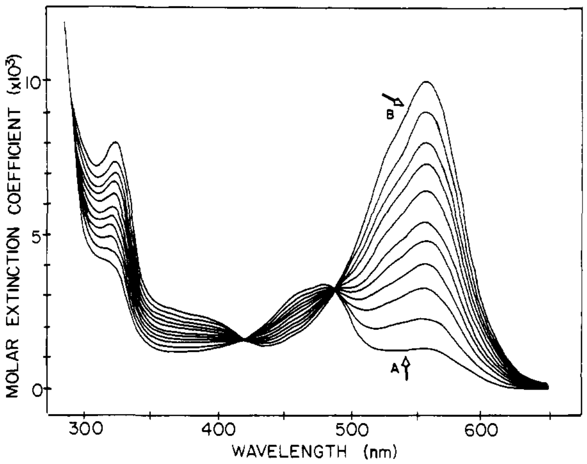

Figure 1. Visible absorption spectrum in acetonitrile as a function of irradiation time for the photochromic reaction **2** → **1**. Curve A is the initial curve, the solvolyzed complex **2**. Curve B is the final curve, corresponding to complex **1**.

15 cycles followed by increasingly limited reversibility until the 20th cycle, whereupon no color change occurs during irradiation. Convincing structural evidence for **2** was obtained from the pyridine reaction which yields a crystalline product. Solvolysis in pyridine also appears to be occurring, as evidenced by the free carbonyl band at 1690 cm^{-1} in the infrared. Unlike the dimethyl sulfoxide and acetonitrile cases the process is irreversible. Elemental analysis is in agreement with two pyridines per platinum which, along with solution conductivity data, suggests both aldehyde and chloride displacement.[5] In an effort to trap the free carbonyl by a strongly coordinating ligand, **1** was treated with a 1:1 molar ratio of triphenylphosphine in acetonitrile in the dark. The resulting red crystalline product analyzes for one triphenylphosphine per platinum,[6] and its infrared spectrum indicates the presence of the free carbonyl. A structural determination using X-ray crystallographic methods is currently under way.[6]

The photochromic process encountered in this reaction is related to that observed for chromium,[7,8] cobalt,[9] and rhodium[10] complexes with ethylenediamine. $[Cr(en)_3]^{3+}$, for example, undergoes light-initiated solvolysis in acidic media, resulting in detachment and protonation of an amine end. The complex then proceeds via a thermal route to the diaquo product.[7,8] In similar rhodium(III) complexes monodentate ethylenediamine with either protonated or nonprotonated detached amine is observed depending on the pH.[10] In the ethylenediamine complexes the ethylenediamine, once protonated, does not close to form the bidentate ligand.

Also unlike the ethylenediamine complexes, the pendant ligand in **2** becomes attached in the presence of light, while the solvent molecule is the photolabile species. Such a process appears to be the reverse of previously studied systems in which the chelating ligand is photolabile and is either completely lost or becomes reattached via a subsequent thermal process. It is possible that the lability of the aldehyde to solvolysis in **1** is promoted by the trans imine, reminiscent of the conjugate base mechanism in the solvolysis of octahedral amine complexes. A contributing factor to lability may also involve the strength of Pt–O vs. Pt–NH bonds. The X-ray data for **1** do show a significant difference in the Pt–O and Pt–NH bond lengths (2.01 (1) and 1.93 (2) Å, respectively) which could be a reflection of relative bond strengths.[1] The mechanistic pathway, as is common in square-planar substitutions, most probably involves a five-coordinate intermediate in the thermal solvolysis and possibly in the photosubstitution. The term "swinging gate" aptly describes the reaction in view of the on-again–off-again nature of the aldehyde. Similar processes could play major roles in template mechanisms whereby condensations may occur only on the uncoordinated or "open gate" ends of chelated ligands. Further investigations of this and related systems are currently in progress.

Acknowledgment. We thank Professor Richard Givens for helpful discussions on the photochemistry. K.B.M. acknowledges the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Kansas, general research allocation No. 3227-XO-0038, for support of this research.

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(5) Anal. Calcd for $PtClON_2C_{24}H_{21}{\cdot}H_2O$: C, 45.75; H, 3.68; N, 8.89; Found: C, 45.54; H, 3.92; N, 8.90. $\Lambda_m(CH_3OH) = 107\ \Omega^{-1}\ cm^2\ mol^{-1}$. A 1:1 electrolyte in CH_3OH ranges from 80 to 115 $\Omega^{-1}\ cm^2\ mol^{-1}$ (Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81–122).

(6) Anal. Calcd for $PtClPON_2C_{32}H_{26}$: C, 53.67; H, 3.66; N, 3.91; Found: C, 53.98; H, 4.28; N, 3.91. The complex crystallizes in the space group *C*2/*c* with unit cell $a = 35.75$ (9), $b = 10.04$ (2), $c = 19.71$ (6) Å, $\beta = 118.5(2)°$, $\rho_{calcd} = 1.70\ g\ cm^{-1}$ (flotation $CHCl_3$–CH_2I_2), and $\rho_{obsd} = 1.67\ g\ cm^{-1}$ for $Z = 8$.

(7) Schläfer, H. L.; Kling, O. *Z. Anorg. Allg. Chem.* **1956**, *287*, 296-312.

(8) Geis, W.; Schläfer, H. L. *Z. Phys. Chem.* (*Wiesbaden*) **1969**, *65*, 107–118.

(9) Kelly, T. L.; Endicott, J. F. *J. Phys. Chem.* **1972**, *76*, 1937–1946.

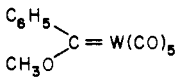
(10) Petersen, J. D.; Jakse, F. P. *Inorg. Chem.* **1977**, *16*, 2845–2848.

Induction of Olefin Metathesis by Acetylenes

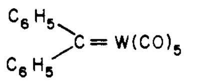
Sir:

If the reason that metal carbenes polymerize acetylenes[1] is that the transformations involve the steps in Scheme I,[1,2] then combining metal carbenes and acetylenes should generate other, possibly more reactive metal carbenes that might initiate transformations their precursors could not. We recently discovered that acetylenes can induce olefin metatheses,[3,4] and we are reporting here how the process can be made to work generally and remarkably stereospecifically. We have discovered that acetylenes not only induce the reactions but quench them as well, and in an accompanying paper we analyze why.[5]

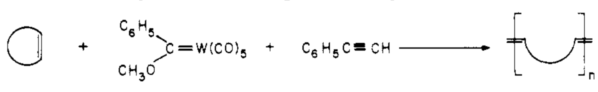
Table I shows that if 200 equiv of three cycloalkenes are combined with 1 equiv of (phenylmethoxycarbene)pentacarbonyltungsten (**1**),[6] no polyalkenamers[1a,7] form, but if phenylacetylene is present, the reactions (eq 1) do indeed take place, even if slowly. However, preliminary attempts to effect the analogous transformation with the seemingly related molecule *cis*-2-pentene were ineffective, even when larger amounts of acetylene and large amounts of metal carbenes were used as



1



2



(1)

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(1) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.

(2) Masuda, T.; Sasaki, N.; Higashimura, T. *Macromolecules* **1975**, *8*, 717.

(3) (a) Katz, T. J. *Adv. Organomet. Chem.* **1977**, *16*, 283. (b) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1. (c) Rooney, J. J.; Stewart, A. *Catalysis* (*London*) **1977**, *1*, 277. (d) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449. (e) Haines, R. J.; Leigh, G. J. *Chem. Soc. Rev.* **1975**, *4*, 1. (f) Mol, J. C.; Moulijn, J. A. *Adv. Catal.* **1975**, *24*, 131.

(4) Some of the results were discussed at the 3rd NSF Workshop on Organometallic Chemistry, Pingree Park, CO, July 16, 1979, and at the 3rd International Symposium on Olefin Metathesis, Lyons, France, Sept 12, 1979. See Katz, T. J.; Lee, S. J.; Shippey, M. A. *J. Mol. Catal.* **1980**, *8*, 219.

(5) Katz, T. J.; Savage, E. B.; Lee, S. J.; Nair, M. *J. Am. Chem. Soc.* **1980**, *102*, following paper in this issue.

(6) (a) Fischer, E. O.; Maasboel, A. *Chem. Ber.* **1967**, *100*, 2445. (b) Aumann, R.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 878. (c) Darensbourg, D. J. *Inorg. Chem.* **1970**, *9*, 32.

(7) Dall'Asta, G. *Rubber Chem. Technol.* **1974**, *47*, 511.

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Scheme I

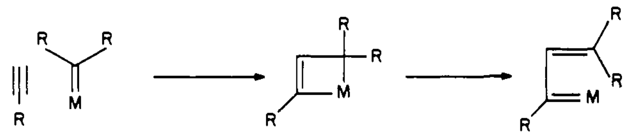

Table I. Yields of Polyalkenamers Obtained in Metatheses Induced by Combining Cycloalkenes (200 equiv), Phenylacetylene (10 equiv), and Metal Carbenes 1 (1 equiv) at 50 °C[a]

cycloalkene[b]	time, days	yield,[c,d] %
5	7	19
7	13	16
8	24	7

[a] In the absence of phenylacetylene, the three cycloalkenes after 7, 26, and 24 days, respectively, gave no polyalkenamers. [b] Number of carbons. [c] The yields are those of the polyalkenamers isolated by dissolving the reaction products in CH_2Cl_2, precipitating with CH_3OH, and drying in a vacuum. They may be in error by ~20% (relative). [d] After 5 days neither cycloheptene nor cyclooctene polymerized appreciably (<~6%), for the reaction mixtures were not yet significantly viscous.

Table II. Yields and Molecular Weights of Products Obtained in Metatheses Induced by Combining Olefins (100 equiv), Phenylacetylene (1 equiv), and Metal Carbene 1 (1 equiv) at 50 °C

olefin	time, days	yield, %	$\overline{M}_w \times 10^{-3}$ [a]	$\overline{M}_n \times 10^{-3}$ [a]
cycloheptene	2	16[b]	321	135
cyclooctene	3.5	8[b]	281	147
cis-2-pentene	7	7.9[c]		

[a] Molecular weights were analyzed by gel-permeation chromatography in toluene on Waters Associates μ-styragel. The values recorded are half the weights of the polystyrenes that would exhibit the chromatograms observed (see ref 5 and 9). [b] Plus or minus ~20% (relative). [c] 100(moles of butene + moles of hexene)/moles of pentene. The error is ~4% (relative).

initiators. Thus 200 equiv of phenylacetylene and 7 equiv of **1** after 6 days at 50 °C converted 100 equiv of *cis*-2-pentene into less than 0.5 equiv of the butenes plus hexenes although 67% of the phenylacetylene was transformed and isolated as its polymer.

The key to bringing about the reactions more efficiently, it turns out, is to use less (not more) of the acetylene. Figure 1 illustrates this for combinations of cyclopentene (100 equiv), phenylacetylene (varying amounts), and metal carbene **1** (1 equiv); it shows that the inverse of the yield of polypentenamer increases linearly with the concentration of phenylacetylene.[8] Notice according to this graph that to achieve a 100% yield one simply has to use no phenylacetylene at all!

Similar increases in yields with decreasing acetylene concentration have been measured for other olefins and are illustrated by the enhanced rates of conversion (compared to the ones described above) in Table II.

These metatheses can be very highly stereoselective.[10] For cycloheptene (IR analysis,[11] 97 ± 1% cis; ^{13}C NMR,[12] >96%),[14] cyclooctene (IR, 94.3 ± 2% cis; ^{13}C NMR, 94 ± 1%),[15] and *cis*-2-pentene (2-butene, 96.5 ± 0.6% cis, 3-hexene 93.7 ± 0.8% cis),[18] although not for cyclopentene (IR, 74 ± 8% cis; ^{13}CNMR, 58%),[20] the stereoselectivities are substantially higher than for every other initiator previously studied, with one significant exception, (diphenylcarbene)pentacarbonyltungsten (**2**).[9,19] This is a remarkable observation, yet it agrees with the introductory premise because the effect of the transformation in Scheme I is to convert metal carbene **1** into a substance whose structure is essentially that of **2**. The acetylene is thus an activator, but unlike the organometallic cocatalysts like $C_2H_5AlCl_2$, which it replaces,

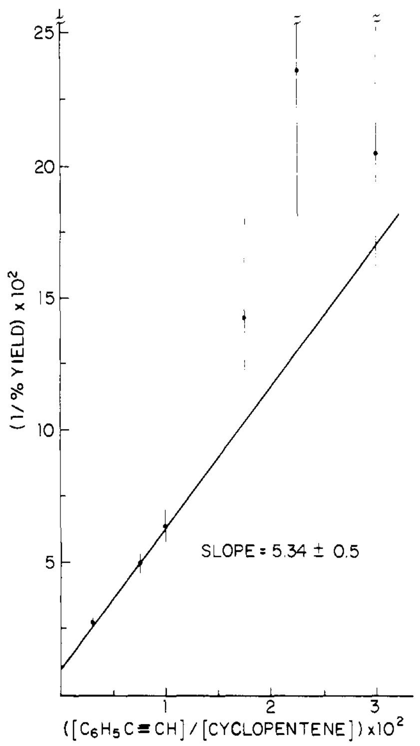

Figure 1. Inverse of the yield of polypentenamer as a function of the ratio of phenylacetylene and cyclopentene. Cyclopentene (100 equiv), phenylacetylene (varying amounts), and **1** (1 equiv) were combined at 50 °C for 21.5 h. The bars show the errors introduced if the weight of the polymer obtained from 680 mg of cyclopentene is measured incorrectly by 10 mg. The yield (100%) at [phenylacetylene] = 0 is derived from theory (see ref 5). The slope and standard deviation are those of the least-squares straight line through the first four points, weighted as the inverse of the relative errors in the inverse yields. The last three points were discarded because when the yields and molecular weights are low, the fraction of polymer lost in the isolation can be high. (These points therefore all appear above the line.)

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[8] The form of this relationship is discussed in ref 5.

[9] Katz, T. J.; Lee, S. J.; Acton, N. *Tetrahedron Lett.* **1976**, 4247.

[10] One set of examples was prepared by combining 100 equiv of each olefin, 1 equiv of acetylene, and 1 equiv of **1** at 50 °C. Other samples were prepared by using somewhat different ratios, and for cyclooctene and cycloheptene some were prepared at 65 °C. No obvious difference was noticed in the measurements of their stereochemistries, which are averaged here.

[11] Measured by the ratio of the intensities of the infrared peaks at 1400 and 960 cm^{-1}. See ref 9, footnote 16.

[12] The intensities of the trans and cis C-2 resonances (see ref **9**, the references in its footnote 18, and ref 13) were measured, and for polyoctenamer those of the two olefinic carbon resonances as well.

[13] (a) Carmen, C. J.; Wilkes, C. E. *Macromolecules* **1974**, *7*, 40. (b) Chen, H. Y. *Appl. Polym. Spectrosc.* **1978**, *7*.

[14] Except in ref 9, polyheptenamer has previously been obtained 6–39% cis in 3–18% yield: (a) Natta, G.; Dall'Asta, G.; Bassi, I.; Carella, G. *Makromol. Chem.* **1966**, *91*, 87. (b) Porri, L.; Diversi, P.; Lucherini, A.; Rossi, R. *Ibid.* **1975**, *176*, 3121. (c) British Patent 1 062 367, 1967.

[15] WCl_6 (or in one case a tungsten carbene) + organoaluminum compounds have given polyoctenamers that are largely trans.[14a,b,16] At low temperatures in the presence of certain modifiers [$BF_3(C_2H_5)_2O$ at −30 °C or diisobutylaluminum oxide at +12 °C] or when WF_6 is used in place of WCl_6, the polymer formed is said to be largely cis.[17]

[16] (a) Calderon, N.; Morris, M. *J. Polym. Sci., Part A-2* **1967**, *5*, 1283. (b) Hoecker, H.; Musch, R. *Makromol. Chem.* **1974**, *175*, 1395. (c) Arlie, J.-P.; Chauvin, Y.; Commereuc, D.; Soufflet, J.-P. *Ibid.* **1974**, *175*, 861.

[17] (a) Syatkowsky, A. I.; Denisova, T. T.; Ikonitsky, I. V.; Babitsky, B. D. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 3939. (b) Zimmerman, M.; Lehnert, G.; Maertens, D.; Pampus, G. German Offen. 2 334 604, 1975. (c) Dall'Asta, G.; Manetti, R. Italian Patent 932 461, 1971, mentioned in ref 7, p 551. (d) Castner, K. F. U.S. Patent 4 038 471, 1977; *Chem. Abstr.* **1978**, *87*, 152726a.

[18] The stereochemistries were measured for the reactions of 2-pentene when the extents of metathesis were between 6 and 8%. Except in ref 19, 2-butene has never been obtained more than 83% cis (and that only at "zero time"; more commonly it is 58% cis at zero time). The 3-hexene is formed even less stereospecifically. See the references in footnote 2 of ref 19. Also: (a) Leconte, M.; Basset, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7296. (b) Leconte, M.; Ben Taarit, Y.; Bilhou, J. L.; Basset, J. M. *J. Mol. Catal.* **1980**, *8*, 263.

[19] Katz, T. J.; Hersh, W. H. *Tetrahedron Lett.* **1977**, 585.

[20] The polypentamer formed by **2** is, as here, not as highly cis as the other polyalkenamers.[9]

it is unique in operating in the absence of strong Lewis acid metal halides, whose presence may account for why most metatheses are only weakly stereoselective[19,21] and for why some are accompanied by undesirable side reactions.[22]

The observation that acetylenes induce metatheses supports the idea that acetylene polymerization like olefin metathesis involves the addition of metal carbenes to carbon–carbon multiple bonds. The observation that acetylenes quench metatheses too is also in accord with the hypothesis as analyzed in the following paper.[5]

Acknowledgment. We are grateful for the support of the National Science Foundation (CHE-77-22726) and the U.S. Office of Naval Research.

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(21) For additional indications that the stereoselectivity of cyclopentene's metathesis falls with added aluminum compounds and with temperature see: (a) Ivin, K. J.; Laverty, D. T.; Rooney, J. J. *Makromol. Chem.* **1977**, *178*, 1545. (b) Oreshkin, I. A.; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1977**, *26*, 2377; *Eur. Polym. J.* **1977**, *13*, 447.

(22) (a) Hocks, L.; Noels, A.; Hubert, A.; Teyssie, P. *J. Org. Chem.* **1976**, *41*, 1631 references therein. (b) Wolovsky, R.; Moaz, N.; Nir, Z. *Synthesis* **1970**, *2*, 656. (c) Graham, J. R.; Slaugh, L. H. *Tetrahedron Lett.* **1971**, 787. (d) Zowade, T.; Hoecker, H. *Makromol. Chem.* **1973**, *165*, 31. (e) Wang, J. L.; Menapace, H. R. *J. Org. Chem.* **1968**, *33*, 3794. (f) Menapace, H. R.; Maly, N. A.; Wang, J. L.; Wideman, L. G. *Ibid.* **1975**, *40*, 2983. (g) Vialle, J.; Basset, J. M. *React. Kinet. Catal. Lett.* **1975**, *2*, 397.

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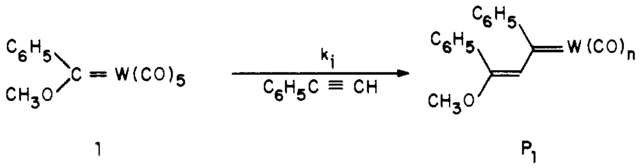
Reactivities of Metal Carbenes toward Alkenes and Alkynes

Sir:

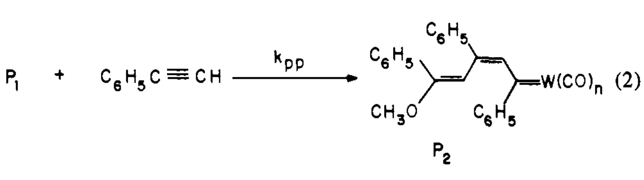
In this paper we report data that show stabilized metal carbenes react much faster with acetylenes than with alkenes, while unstabilized metal carbenes select oppositely. These data were obtained in accounting for acetylenes both inducing an otherwise ineffective metal carbene to initiate olefin metathesis and also quenching the reaction.[1]

We suppose that a metal carbene combines with an acetylene (like phenylacetylene) according to Scheme I of the preceding paper,[1] transforming the initial metal carbene **1** into P_1 (eq 1).



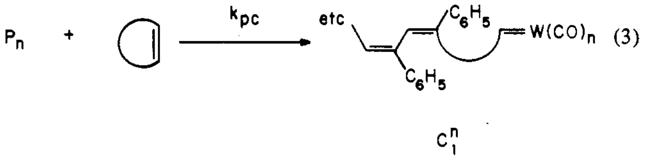
(1)

P_1 then reacts with more of the acetylene according to eq 2; P_2



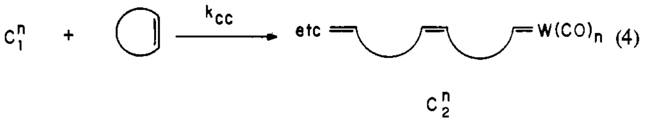
(2)

or a higher homologue, P_m, reacts with the olefin, say a cycloalkene, giving C_1 (eq 3); C_1 then propagates the metathesis in the usual way (eq 4).



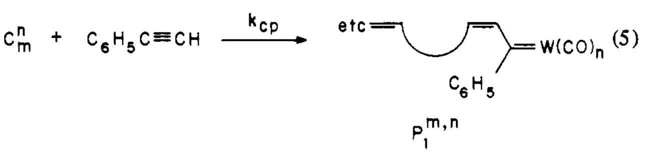
(3)

We suppose that eq 5, a plausible analogue of the



(4)

transformations above, whose action is essentially the reverse of eq 3, accounts for the quenching.



(5)

Figure 1, depicting gel-permeation chromatograms of polymers formed from cyclopentene and varying amounts of phenylacetylene, supports these ideas, for the intensity of absorption of 400-nm light (which measures poly(phenylacetylene) units[2] but not polyalkenamers[3]) parallels the intensity of refractive-index changes (which measures the amount of bulk polymer, manily polyalkenamer), implying that poly(phenylacetylene) and polyalkenamer units are attached.

An alternative theory for the quenching, involving either the acetylene or its polymer combining with **1**, destroying its initiating ability, and thereby decreasing the number of polymer chains, might accommodate this observation, but it cannot be correct because, as Figures 1 and 2 show, the molecular weights do not increase with phenylacetylene concentration as they should.[5] However, if eq 5 applies and growing polyphenylacetylenes terminate easily (which seems plausible since polyacetylenes are commonly found to have much lower molecular weight[6,7] than polyalkenamers[4,9]), then capping a growing polyalkenamer with a phenylacetylene will indeed increase the probability of its early termination.

The chromatograms also provide data for quantitative analyses of the equations. They are bimodal (presumably the high molecular weight material is largely polypentenamer[9] and the low molecular weight material poly(phenylacetylene)[6]), and, as summarized in Table I, the ratio of the areas under the high and low

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(1) Katz, T. J.; Lee, S. J.; Nair, M.; Savage, E. B. *J. Am. Chem. Soc.* **1980**, *102*, preceding paper in this issue.

(2) The electronic spectrum is published in Masuda, T.; Sasaki, N.; Higashimura, T. *Macromolecules* **1975**, *8*, 717.

(3) The polypentenamer obtained by using (diphenylcarbene)pentacarbonyltungsten as the initiator (ref 4) exhibits asborption <100 times as intense at 400 nm.

(4) Katz, T. J.; Lee, S. J.; Acton, M. A. *Tetrahedron Lett.* **1976**, 4247.

(5) They decrease also when phenylacetylene (10 mol) is added to (diphenylcarbene)pentacarbonyltungsten (1 mol) and cyclopentene (100 mol) from $\bar{M}_w = 5.3 \times 10^5$, $\bar{M}_n = 3.1 \times 10^5$ to $\bar{M}_w = 4.6 \times 10^4$, $\bar{M}_n = 1.7 \times 10^4$. The reactions were effected at 40 °C for 16 h, and the yields of polypentenamer were 46% and 22%.

(6) $\bar{M}_n$'s for poly(phenylacetylene) made in a number of ways with metal catalysts range from about 1000 to 15 000 and are commonly around 7000.[2,7,8]

(7) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.

(8) Inter alia: (a) Kern, R. J. *J. Polym. Sci., Part A-1* **1969**, *7*, 621. (b) Kushnerev, M. I.; Bantzirev, G. I.; Cherkashin, M. I.; Berlin, A. *Bull. Acad. Sci. USSR* **1971**, *20*, 2161. (c) Simionescu, C. I.; Percec, V.; Dumitrescu, S. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2497. (d) Biyani, B.; Campagna, A. J.; Daruwalla, D.; Srivastava, C. M.; Ehrlich, P. *J. Macromol. Sci. Chem.* **1975**, *A9*, 327. (e) Nguyen, H. X.; Amdur, S.; Ehrlich, P. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1977**, *18*, 200. (f) Masuda, T.; Thieu, K.-Q.; Higashimura, T. *Polym. J.* **1978**, *10*, 269. (g) Woon, P.S.; Farona, M. F. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1749.

(9) Polyalkenamers have molecular weights that are usually between 10^5 and 10^6 (see ref 4 and 10).

(10) Inter alia: (a) Witte, J.; Hoffmann, M. *Makromol. Chem.* **1978**, *179*, 641. (b) P. Günther et al. *Angew. Makromol. Chem.* **1970**, *14*, 87. (c) Glenz, W.; Holtrup, W.; Küpper, F. W.; Meyer, H. H. *Ibid.* **1974**, *37*, 97. (d) Calderon, N.; Ofstead, E. A.; Judy, A. W. *J. Polym. Sci., Part A* **1967**, *5*, 2209. (e) Arlie, J.-P.; Chauvin, Y.; Commereuc, D.; Soufflet, J.-P. *Makromol. Chem.* **1974**, *175*, 861.

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