following direct adsorption of acetaldehyde on the zeolite catalysts.[11] Further exposure of the catalyst to the atmosphere allowed the acetaldehyde to diffuse out and permitted a spectrum of the tars to be obtained (Figure 2c). Alternatively, further heating of adsorbed acetaldehyde in the presence of oxygen resulted in the formation of acetic acid (Scheme I).

Control experiments in which water was coadsorbed onto the zeolite with acetylene yielded spectra similar to Figure 2b. The highly paraffinic nature of these tars suggests that the required source of hydrogen may be water. Indeed, in samples that were not deliberately exposed to water, the amount of tars formed correlated with the catalyst activation temperature and thus the degree to which water was present in the catalyst. Furthermore, similar tars were observed to form when authentic samples of acetaldehyde on HY catalyst were subjected to analogous high-temperature studies.[12]

The dynamics of V were probed by dipolar dephasing[13] experiments at 298 and 143 K. At 298 K, the 143-ppm peak survived 50 μs of interrupted decoupling. At 143 K, however, the intensity of the 143-ppm peak was greatly attenuated. The 107-ppm resonance was completely suppressed at both temperatures. These results suggest that V undergoes rapid rotation at 298 K about the C–O axis, with the effect that the dipolar coupling to the directly bound proton is attenuated.[14] At low temperatures, this rotation is slowed down, and the 143-ppm peak is attenuated.

**Acknowledgment.** This work was supported by a grant from the National Science Foundation (Grant CHE8700667). E.J.M. is a National Science Foundation Predoctoral Fellow. J.L.W. and M.L. are Department of Education Fellows.

**Registry No.** $H_2O$, 7732-18-5; $CH_3CHO$, 75-07-0; acetylene, 74-86-2; alumina, 1344-28-1.

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[11] The chemistry is analogous to the hydrolysis of vinyl ethers. See, for example: Salomaa, P. In *The Chemistry of the Carbonyl Group*; Patai, S., Ed.; Interscience: New York, 1966.

[12] Chang and Silvestri also observed the conversion of acetaldehyde to alkyl aromatics: Chang, C. D.; Silvestri, A. J. *J. Catal.* **1977**, *47*, 249.

[13] Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854.

[14] Elementary considerations of the bond angles for $sp^2$ carbons suggest that the angle between the C–H bond vector for the carbon attached to oxygen in species V and the axis of rotation (the C–O bond vector) is 60°, which is close to the "magic angle" of 54.7°, which is effective in averaging dipolar couplings.

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# Photoreduction of Palladium Radical Cations. Transient Absorbance Kinetics of Electron Transfers to Photogenerated $[Pd(CNMe)_3]^{\bullet +}$ Radicals

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The photochemical deposition of metal films provides the basis for a wide variety of imaging processes.[3] Laser direct writing of conducting metal features has received considerable attention as a means of defining and "wiring" a micron-scale circuit in a single step.[4-6] We report the photoreduction of organometallic radical cations by electron transfers to photogenerated $[Pd(CNMe)_3]^{\bullet +}$ radicals. It is generally recognized that photogenerated $^{\bullet}ML_n$ radicals are potentially stronger both as oxidants and as reductants than their parent ground-state, metal–metal-bonded $L_nM–ML_n$ complexes.[7-9] The complex $[Pd_2(CNMe)_6][PF_6]_2$ (**1**) was found previously to exhibit photochemical $\sigma,\sigma^*$ Pd–Pd bond homolysis.[9,10] Photogenerated $[Pd(CNMe)_3]^{\bullet +}$ radicals derived from photolysis of **1** are rapid and potent reductants of a variety of electron acceptors,[9] A, eq 1. We now report our findings

$$[Pd(CNMe)_3]^{\bullet +} + A \xrightarrow[\text{solvent}]{k_e} [Pd(CNMe)_3(\text{solvent})]^{2+} + A^{\bullet -} \qquad (1)$$

relating to the role of $[Pd(CNMe)_3]^{\bullet +}$ radicals as photogenerated oxidants. The $[Pd(CNMe)_3]^{\bullet +}$ radical system provides a rare example for direct observation of both reductive and oxidative behavior of an organometallic radical. A key finding is that transfer of an electron to the $d^9$, Pd(I) radical produces a Pd(0) complex which spontaneously deposits palladium as a metal film.

**Table I.** Electron-Transfer Rate Constants for the Reduction of $[Pd(CNMe)_3]^{\bullet +}$ by Substituted Ferrocenes with Determined $E_{1/2}$ Values

| ferrocene | $E_{1/2}$, V vs SCE | $[Pd(CNMe)_3]^{\bullet +}$ $k_e$, $M^{-1}$ $s^{-1}$ |
|---|---|---|
| $Fe(C_5Me_5)_2$ | −0.09 | $9 \times 10^7$ |
| $Fe(C_5H_5)(C_5Me_5)$ | +0.13 | $6 \times 10^7$ |
| $Fe(C_5H_4Me)_2$ | +0.31 | $3 \times 10^7$ |
| $Fe(C_5H_5)(C_5H_4CH_2OH)$ | +0.38 | $3 \times 10^6$ |
| $Fe(C_5H_5)_2$ | +0.42 | $2 \times 10^6$ |
| $Fe(C_5H_4I)(C_5H_5)$ | +0.54 | $5 \times 10^4$ |
| $Fe(C_5H_4Cl)_2$ | +0.77 | $<4 \times 10^4$ |

Irradiation (λ = 313 nm) of an acetonitrile solution of **1** (0.013 mmol) and $Fe(C_5Me_5)_2$ (0.027 mmol) leads to the disappearance of **1** at 307 nm and the appearance of a band at 777 nm characteristic of $[Fe(C_5Me_5)_2]^{\bullet +}$, as observed by UV–vis spectrophotometry. A new absorbance at 410 nm also appears and corresponds to $[Pd(CNMe)_2]_n$.[11,12] This band vanishes over a period of several minutes as metallic palladium is deposited within the quartz photolysis cell. We note that palladium(0) isocyanide oligomers $[Pd(CNR)_2]_n$ (R = $Pr^i$, $C_6H_{11}$, Ph, p-$MeC_6H_4$, p-$MeOC_6H_4$) are known to decompose in polar solvents.[11,12] Irradiation of an identical sample at 438 nm, within the $Fe(C_5Me_5)_2$ absorbance band, produced no reaction. Similarly, no reaction was observed in refluxed samples of **1** and $Fe(C_5Me_5)_2$. These results indicate that decamethylferrocene is oxidized by photolysis of **1**, producing a Pd(0) isocyanide species which is unstable in acetonitrile with respect to the formation of palladium metal.

Laser flash photolysis (7 ns, 355 nm) of **1** (1 mM in acetonitrile) produces an intense transient absorbance at 405 nm. The disappearance of transient absorbance corresponds to second-order recombination of $[Pd(CNMe)_3]^{\bullet +}$ radicals (eq 2). Recombination

$$2[Pd(CNMe)_3]^{\bullet +} \xrightarrow{k_r} \underset{\mathbf{1}}{[Pd_2(CNMe)_6]^{2+}} \qquad (2)$$

of $[Pd(CNMe)_3]^{\bullet +}$ radicals occurs with a rate constant, $k_r = 1 \times 10^9$ $M^{-1}$ $s^{-1}$, near the diffusion-controlled limit in acetonitrile.[9] The addition of decamethylferrocene (10 μM) to a solution of **1** (1 mM in acetonitrile) dramatically accelerates the observed rate of disappearance of $[Pd(CNMe)_3]^{\bullet +}$ radicals. The synchronous appearance of the decamethylferricinium ion indicates that the disappearance of $[Pd(CNMe)_3]^{\bullet +}$ is due to electron transfer. The kinetics of electron transfer to photogenerated $[Pd(CNMe)_3]^{\bullet +}$ radicals was examined for each of the ferrocenes, $Fe(C_5Me_5)_2$, $Fe(C_5H_5)(C_5Me_5)$,[13] $Fe(C_5H_4Me)_2$, $Fe(C_5H_5)(C_5H_4CH_2OH)$,

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[2] Research Fellow of the Alfred P. Sloan Foundation, 1987-1991.

[3] *Proceedings of the Seventh International Symposium on the Photochemistry of Coordination Compounds*; Yersin, H., Vogler, A., Eds.; Springer-Verlag: Berling, Heidelberg, 1987.

[4] Ehrlich, D. J.; Tsao, J. Y. *J. Vac. Sci. Technol., B* **1983**, *1*, 969.

[5] Montgomery, K. R.; Mantei, T. D. *Appl. Phys. Lett.* **1986**, *48*, 493.

[6] (a) Gross, M. E.; Appelbaum, A.; Gallagher, P. K. *J. Appl. Phys.* **1987**, *61*, 1628. (b) Harriott, L. R.; Cummings, K. D.; Gross, M. E.; Brown, W. L. *Appl. Phys. Lett.* **1986**, *49*, 1661.

[7] Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187.

[8] Hepp, A. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1981**, *103*, 1258.

[9] Metcalf, P. A.; Kubiak, C. P. *J. Am. Chem. Soc.* **1986**, *108*, 4682.

[10] Reinking, M. K.; Kullberg, M. L.; Cutler, A. R.; Kubiak, C. P. *J. Am. Chem. Soc.* **1985**, *107*, 3517.

[11] Malatesta, L. *J. Chem. Soc.* **1955**, 3924.

[12] Fischer, E. O.; Werner, H. *Chem. Ber.* **1962**, *95*, 703.

0002-7863/90/1512-4052$02.50/0

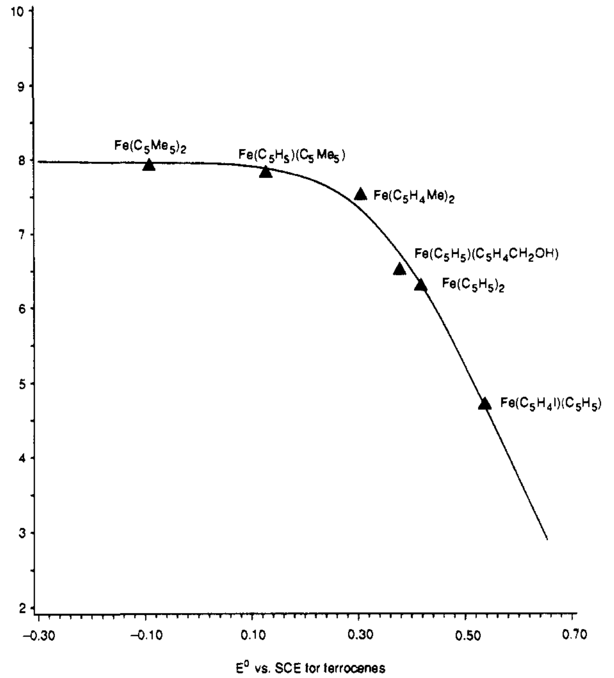

**Figure 1**. Log plot of $k_e^{obsd}$, the rate constant for electron transfer from differently substituted ferrocenes to photogenerated palladium(I) radicals vs $E°$(ferricinium/ferrocene). The curve represents a fit of the complete Marcus/Agmon–Levine expression for the electron-transfer cross reaction.[16,17]

$Fe(C_5H_5)_2$, $Fe(C_5H_4I)(C_5H_5)$, and $Fe(C_5H_4Cl)_2$,[14,15] by laser flash photolysis. The rate constants for electron transfer from the differently substituted ferrocenes for photogenerated $[Pd(CNMe)_3]^{\bullet+}$ radicals are summarized in Table I. The electron-transfer rate constants clearly depend on potentials for ferricinium ion formation. Rate constants, $k_e^{obsd}$, for electron transfer increase as the ferrocenes become progressively easier to oxidize and converge on a value of $\sim 10^8$ $M^{-1}$ $s^{-1}$ for decamethylferrocene, $E°(Fe(C_5Me_5)_2^{+/0}) = -0.09$ V vs SCE.

A log plot of the observed electron-transfer rate constants vs $E°$ (ferricinium/ferrocene) is presented in Figure 1. The rate constant for dichloroferrocene, the ferrocene most stable to oxidation, $E°(Fe(C_5H_4Cl)_2^{+/0}) = +0.77$ V vs SCE, was too slow to measure meaningfully ($<4 \times 10^4$ $M^{-1}$ $s^{-1}$). Two aspects of these data are striking. First, rate constants $k_e^{obsd}$ show a monotonic increase with increased driving force for electron transfer (more negative $E°$(ferricinium/ferrocene)) until a saturation limit is approached at $E°$(ferricinium/ferrocene) $\simeq +0.3$ V vs SCE, Figure 1. Second, the limiting rate constants, $k_e^{obsd}$, for the most exoergic electron transfers, $E°$(ferricinium/ferrocene) = −0.09 – 0.30 V vs SCE, approach values of only $\sim 10^8$ $M^{-1}$ $s^{-1}$. These limiting rate constants, $k_e^{obsd}$, are 2 orders of magnitude less than the diffusion limit in in acetonitrile.[18] Within the context of the Marcus[19]/Agmon–Levine[20] model for electron transfer, there are two possible sources of the observed rate saturation: (1) nonadiabaticity resulting from poor electronic coupling between the photogenerated $[Pd(CNMe)_3]^{\bullet+}$ radical and the electron donor ferrocene;[16] (2) preequilibrium changes in one of the reactants leading to observed rate constants, $k_e^{obsd} = P_1{}^*k_e$, modulated by the preequilibrium constant, $P_1{}^*$.[21] We have examined both of these possibilites. Effects of nonadiabaticity may be described by the kinetic equation of Balzani et al.[16] or the equivalent expression of Meyer et al.[22] A fit of our data to this model produced values of the intrinsic barrier, $\Delta G^*(0) = 1.3$ kcal/mol and $E°(Pd(CNMe)_3^{+/0}) = +0.35$ V vs SCE. Inasmuch as the intrinsic barrier is unrealistically lower than the value determined for ferrocene self-exchange alone,[23] we reject the nonadiabaticity hypothesis. We have linearized our observed electron-transfer data, $k_e^{obsd}$, within a preequilibrium model by constraining the diffusion-corrected $k_e^{obsd}$ to the Marcus condition: $RT \ln (k_e/(k_{22}(\text{ferrocene})^{1/2}))$ vs $E°$(ferricinium/ferrocene) is linear with slope = $-^1/_2$. Details may be found in supplementary material. Our studies suggest the *preequilibrium dissociation of methyl isocyanide is required for palladium radical reduction*, eqs 3–4.

$$Pd(CNMe)_3{}^{\bullet+} \underset{}{\overset{K_{diss}}{\rightleftharpoons}} Pd(CNMe)_2{}^{\bullet+} + CNMe \qquad (3)$$

$$Pd(CNMe)_2{}^{\bullet+} + e^- \xrightarrow{k_e} Pd(CNMe)_2 \qquad (4)$$

Observed rate constants display an inverse linear dependence on [CNMe], with $K_{diss}/[CNMe] = 0.005$. We note that both the $[Pd(CNMe)_3]^{\bullet+}$ and $[Pd(CNMe)_2]^{\bullet+}$ radicals have been prepared recently in the gas phase and their electron transfers from substituted ferrocenes are under investigation.[24] Interestingly, rates of electron transfer to the less substituted $[Pd(CNMe)_2]^{\bullet+}$ species are significantly faster than those to $[Pd(CNMe)_3]^{\bullet+}$ for all ferrocenes studied; and no $[Pd(CNMe)_4]^{\bullet+}$ is observed in the gas phase. We will report our studies of gas-phase electron transfer separately.

The electron-transfer photochemistry described clearly shows that the photogenerated, dissociated $[Pd(CNMe)_2]^{\bullet+}$ transients are reducible by even modest electron donor ferrocenes. We note that the cyclic voltammogram of **1** at a glassy carbon electrode in acetonitrile exhibits two irreversible reductions at $E = -0.9$ and −1.1 V vs SCE. The photochemical homolysis of the Pd–Pd bond of **1** and dissociation of CNMe together impart at least ~1.25 V of oxidizing potential to the $[Pd(CNMe)_2]^{\bullet+}$ radical. The significant difference between the reduction potential of $[Pd(CNMe)_2]^{\bullet+}$ compared to **1** provides the opportunity for quantum efficient photodeposition of palladium metal. An example of strictly thermal metal–organic chemical vapor deposition (MOCVD) of palladium was recently reported.[25] Pulsed UV irradiation of a glassy carbon electrode at −0.1 V vs SCE in an electrochemical cell containing **1** (1 mM) in 0.1 M $[NBu_4][PF_6]$ led to cathodic transient photocurrents of 0.5 μA and the deposition of palladium metal films *on the electrode surface*. Maximum photocurrents in the absence of **1** were less than 2% of those in the presence of **1**. Analysis by XPS of films deposited onto glassy carbon indicated the presence of metallic palladium ($3d_{5/2}$, 335.8 eV; $3d_{3/2}$, 341.1 eV) of high purity.

These studies demonstrate electron-transfer reduction of a photogenerated metal radical at rates approaching $10^8$ $M^{-1}$ $s^{-1}$ and thereby the preparation of metal films.

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(13) Bunel, E. E.; Valle, L.; Manriquez, L. M. *Organometallics* **1985**, *4*, 1680.

(14) Rausch, M. D.; Ciappenelli, D. J. *J. Organomet. Chem.* **1967**, *10*, 127.

(15) Phillips, L.; Lacey, A. R.; Cooper, M. K. *J. Chem. Soc., Dalton Trans.* **1988**, 1383.

(16) Balzani, V.; Scandola, F.; Orlandi, G.; Sabbatini, N.; Irdelli, M. T. *J. Am. Chem. Soc.* **1981**, *103*, 3370.

(17) Data reduction, curve fitting, and $E°(Pd(CNMe)_2{}^{+/0})$ estimation are described in the supplementary material.

(18) The diffusion-limited rate constant was calculated to be $1.9 \times 10^{10}$ $M^{-1}$ $s^{-1}$ (MeCN, 25 °C) from the Stokes–Einstein equation, $k_D \cong 8RT/3\eta$, where $\eta$ is the viscosity of the solvent. See, for example: Wilkinson, F. *Chemical Kinetics and Reaction Mechanisms*; Van Nostrand Reinhold: New York, 1980.

(19) (a) Marcus, R. A. *J. Chem. Phys.* **1968**, *72*, 891. (b) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679. (c) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(20) (a) Agmon, N.; Levine, R. D. *Chem. Phys. Lett.* **1977**, *52*, 197. (b) Levine, D. R. *J. Phys. Chem.* **1979**, *83*, 159. (c) Agmon, N. *Int. J. Chem. Kinet.* **1981**, *13*, 333.

(21) Marcus, R. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 213.

(22) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815.

(23) McManis, G. E.; Nelson, R. M.; Gochev, A.; Weaver, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5533.

(24) Gord, J.; Freiser, B. S.; Kubiak, C. P., unpublished results.

(25) Gozum, J. E.; Pollina, D. M.; Jensen, J. A. Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 2688.

Professors Dale Margerum and Dave McMillin for helpful suggestions regarding this work.

**Supplementary Material Available:** Plots of transient absorbance vs time and $k_e^{obsd}$ vs [ferrocene] for all ferrocenes studied and description of data reduction (7 pages). Ordering information is given on any current masthead page.

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# Homoconjugated Cyclic Polydiacetylenes[1]

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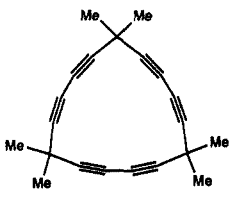
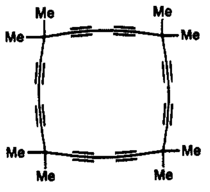
*Received October 23, 1989*

We have prepared and characterized the first cyclic homoconjugated polydiynes (**1**–**4**) and herein report our synthetic routes to these novel compounds, together with some of the properties they exhibit; their UV spectra show a distinct dependence on ring size.



**1**



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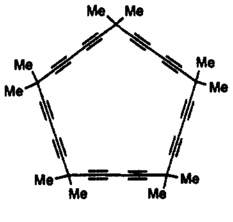

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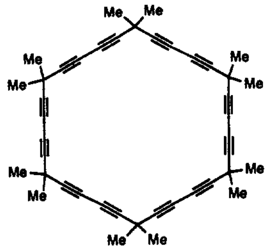


**4**

Earlier work in these laboratories[2-5] has focused on homoconjugated cyclic polyacetylenes bearing a single alkyne unit along each side of the ring ("[*N*]pericyclynes" with *N* = 5–8). Unfortunately, the first two members of that family (*N* = 3 and 4, the lower homologues of compounds **1** and **2** above) have so far escaped synthesis. Even in the larger pericyclynes, however, spectroscopic and thermochemical evidence indicates a strong electronic interaction among the cyclically juxtaposed alkyne units, and a similar degree of cyclic homoconjugation can be expected for the corresponding polydiynes. In compound **1**, bond-angle compression at the saturated carbon atoms should magnify the effect.

**Scheme I**

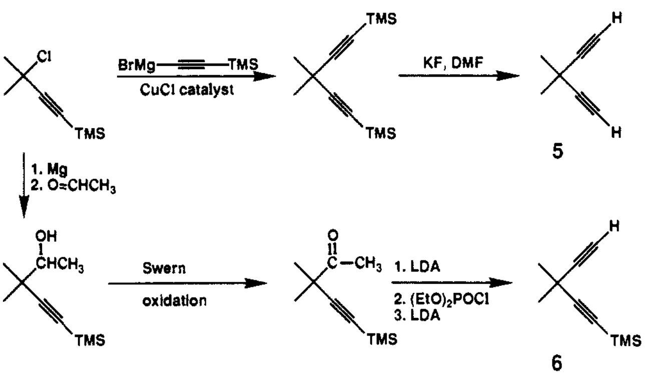


**Table I.** UV Spectra of Homoconjugated Cyclic Polydiacetylenes in Cyclohexane

| compd | $\lambda_{max}$ (ε) |
|---|---|
| 1 | 219 (5170), 237 (2210), 253 (2060), 265 (1050, sh), 277 (760, sh) |
| 2 | 212 (4900), 220 (4160), 232 (3880), 246 (4190), 260 (2150) |
| 3 | 213 (6400), 220 (5840), 232 (5510), 245 (6210), 259 (4660) |
| 4[a] | 213, 220, 231, 245, 259 |

[a] Compound **4** does not dissolve completely in cyclohexane, so ε values are not reliable; however, the spectrum is virtually superimposable on that of compound **3**.

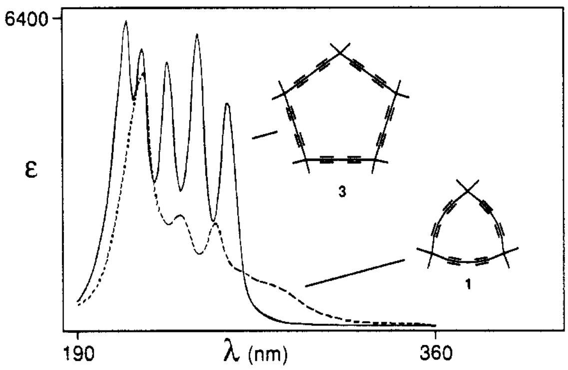
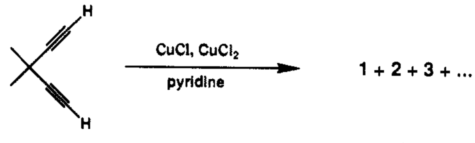


**Figure 1.** UV spectra of compounds **1** and **3** in cyclohexane.

We first prepared these homoconjugated cyclic polydiynes in a one-step "shotgun" synthesis by cyclooligomerization of 3,3-dimethyl-1,4-pentadiyne[6] under conditions known to effect oxidative coupling of terminal acetylenes (eq 1).[7] GC–mass spectral analysis revealed that compounds **1**–**3** were all produced in this reaction, albeit in low yield. Compound **4** (vide infra) does not pass through the gas chromatograph, so higher cyclic oligomers may also be present in this product mixture. The great abundance of easily bent acetylenic carbon atoms presumably accounts for the readiness with which the strained compounds **1** and **2** are formed.



(1)

Following this encouraging preliminary result, we set out to devise more efficient, stepwise syntheses of macrocycles **1**–**4**. Scheme I outlines practical routes we developed to the requisite

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[1] Part 7 in the series "Cyclynes". For part 6, see ref 5. This work was first presented at the 193rd National Meeting of the American Chemical Society, Denver, CO, April 1987.

[2] Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.* **1983**, *105*, 7760.

[3] Scott, L. T.; DeCicco, G. J.; Hyun, J. L.; Reinhardt, G. *J. Am. Chem. Soc.* **1985**, *107*, 6546.

[4] Houk, K. N.; Scott, L. T.; Rondan, N. G.; Spellmeyer, D. C.; Reinhardt, G.; Hyun, J. L.; DeCicco, G. J.; Weiss, R.; Chen, M. H. M.; Bass, L. S.; Clardy, J.; Jørgensen, F. S.; Sarkozi, V.; Petit, C.; Ng, L.; Jordan, K. D. *J. Am. Chem. Soc.* **1985**, *107*, 6556.

[5] Scott, L. T.; Cooney, M. J.; Rogers, D. W.; Dejroongruang, K. *J. Am. Chem. Soc.* **1988**, *110*, 7244.

[6] Diyne **5** has previously been prepared (Herberich, G. E.; Bauer, E.; Hengelsbach, J.; Kolle, U.; Huttner, G.; Lorenz, H. *Chem. Ber.* **1977**, *110*, 760), but we find the synthesis in Scheme I more convenient. All new compounds reported herein have been fully characterized by the usual spectroscopic methods plus elemental analysis and/or high-resolution mass spectrometry. $^{13}$C NMR (CDCl$_3$): (**1**) 94.9, 66.1, 29.2, 27.5; (**2**) 81.3, 66.1, 29.9, 27.3; (**3**) 80.9, 64.9, 29.9, 27.0; (**4**) 80.7, 64.9, 30.3, 26.9.

[7] O'Krongly, D.; Denmeade, S. R.; Chiang, M. Y.; Breslow, R. *J. Am. Chem. Soc.* **1985**, *107*, 5544–5545.

0002-7863/90/1512-4054$02.50/0