atom thereby further polarizing the O–O bond.[6] Other metal ions should also have a similar effect. However, the substitution of $Pd(O_2CC_2H_5)_2$ by either $Pb(O_2CCH_3)_4$, $Fe(O_2CCH_3)_2$, or $Co(O_2CCF_3)_2$[7] resulted in a yield of $CF_3CO_2CH_3$ that was either similar to or only marginally higher than that observed with peroxytrifluoroacetic acid alone. An alternative role of the Pd(II) ion can be envisaged based on our previous observation[8] that the Pd(II) ion will oxidize methane under stoichiometric conditions through a step involving an electrophilic attack on a methane C–H bond (eq 2). A parallel catalytic oxidation pathway may, therefore, ensue upon the addition of the Pd(II) ion to the system. The catalytic cycle would combine the reaction shown in eq 2 with a step involving the reoxidation of Pd(0) to Pd(II) by peroxytrifluoroacetic acid. In principle, it should be possible to initiate the catalytic cycle by starting with Pd(0). The addition of "palladium black" to peroxytrifluoroacetic acid did result in an enhanced yield of $CF_3CO_2CH_3$; nevertheless, the effect was much less than that observed with $Pd(O_2CC_2H_5)_2$ (Figure 1). This observation does not necessarily rule out the above catalytic cycle since, in several catalytic oxidations involving the Pd(II)/(0)/(II) cycle, it has been observed that once Pd(0) is allowed to aggregate, it cannot be easily reoxidized to Pd(II).[9]

$$CH_4 + Pd(O_2CR)_2 \xrightarrow[90\ ^\circ C]{CF_3CO_2H} CF_3CO_2CH_3 + Pd(0) + 2RCO_2H \quad (2)$$

The final point concerns the use of $Pd(O_2CC_2H_5)_2$ for methane oxidation. $Pd(O_2CCH_3)_2$ was also effective in promoting oxidation of methane by peroxytrifluoroacetic acid. However, studies involving $Pd(O_2CCD_3)_2$ indicated that a fraction (15–20%) of the acetate ligand was converted to $CF_3CO_2CD_3$ in the presence of peroxytrifluoroacetic acid. On the basis of previous reports,[10] the following series of steps may be proposed (eq 3).

$$Pd(O_2CCD_3)_2 \xrightarrow{H_2O_2,\ (CF_3CO)_2O} CD_3C(O)OOC(O)CF_3 \rightarrow [CD_3C(O)O^\bullet + {}^\bullet OC(O)CF_3] \xrightarrow{-CO_2} [CD_3^\bullet + {}^\bullet OC(O)CF_3] \rightarrow CD_3OC(O)CF_3 \quad (3)$$

Therefore, in order to remove all ambiguity concerning the source of the methyl group in CF_3CO_2Me, $Pd(O_2CC_2H_5)_2$ was used as the source for the Pd(II) ion. A further advantage of using the propionate salt is that, due to its greater stability, any ethyl radical generated is unlikely to abstract a hydrogen atom from methane to generate the corresponding methyl radical. No $CF_3CO_2CF_3$ was observed when $Pd(O_2CCF_3)_2$ was treated with peroxytrifluoroacetic acid presumably due to the low stability of the trifluoromethyl radical. However, this latter Pd(II) species was not used for methane oxidation due to its insolubility in the reaction medium.

In conclusion, we have demonstrated that it is possible to achieve the selective, catalytic oxidation of methane through an electrophilic pathway under mild conditions.[11] It is worthwhile noting that the biological oxidation of methane[12] also involves a metal-catalyzed reaction of methane with a hydrogen peroxide equivalent (eq 4). In analogy with the biological oxidation of higher hydrocarbons, it has been proposed that the mechanism of methane oxidation involves the intermediacy of a methyl radical.[13] However, the methyl radical is a particularly high energy species, and such a mechanism has never been demonstrated in a nonbiological system, except under photolytic conditions[1] or at very high temperatures.[14] In view of our results, we believe that an alternative electrophilic mechanism should be considered for biological methane oxidations especially since high-valent, electrophilic metal species are believed to be involved.[8a]

$$O_2 + 2H^+ + 2e^- \rightarrow [H_2O_2] \xrightarrow{CH_4} CH_3OH + H_2O \quad (4)$$

Acknowledgment. This research was funded by a grant from the National Science Foundation (CHE-8906587). We thank Johnson Matthey, Inc., for a generous loan of palladium salts.

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A Pd-Catalyzed Zipper Reaction

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Recently, we have focused on developing reactions wherein the product is the simple sum of the reactants.[1] When applied intramolecularly, such reactions become cycloisomerizations.[2-4] Considering the importance of cationic initiated polyolefin cyclizations,[5] the prospect of polyolefin cyclizations catalyzed by transition metals becomes extremely attractive because of the control that transition-metal templates may exercise. In this paper, we report the realization of a polyolefin polycycloisomerization.[6,7]

Our investigation began with the cis-1,4-disubstituted cyclopentene **1**[8] because of its ready accessibility from the monoepoxide of cyclopentadiene using Pd(0) chemistry. Warming a 0.4 M benzene solution of dienyne **1** containing 2.5 mol % $(dba)_3Pd_2 \cdot CHCl_3$, 10 mol % triphenylphosphine, and 10 mol % acetic acid

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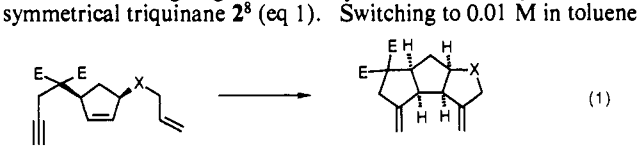
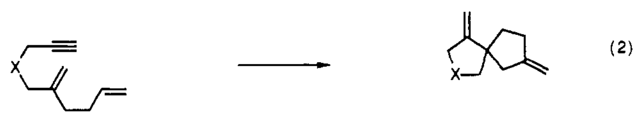
(8) This compound has been characterized spectrally and elemental composition established by combustion analysis and/or high-resolution mass spectroscopy.

at 53 °C overnight gave a 43% yield of the easily identified symmetrical triquinane **2**[8] (eq 1). Switching to 0.01 M in toluene at 105 °C for 4 h increases the yield to 57%. Subjecting the nitrogen substrate **3**[8] to similar conditions provides the azatriquinane **4**[8] in similar yields.

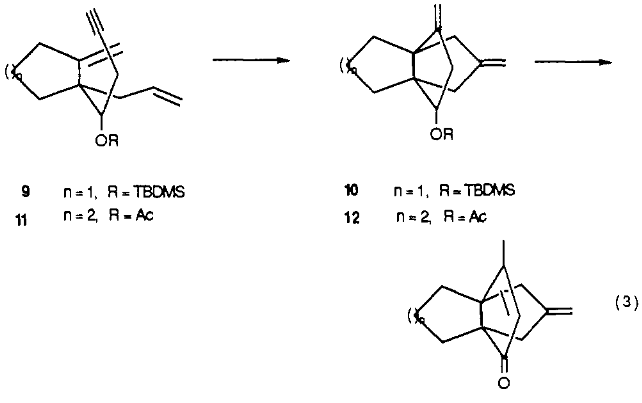


1 X = CE$_2$ **2** X = CE$_2$ E = CO$_2$CH$_3$
3 X = NTs **4** X = NTs

The juxtaposition of the unsaturation determines the ring system being formed. For example, using a 1,1-disubstituted double bond for the central unsaturation as in **5**[8] or **7**[8] creates a spiro-fused system **6**[8] or **8**[8] (eq 2) in 85–89% yields under conditions similar to the above, except that the reactions proceeded at room temperature with tri-*o*-tolylphosphine as the preferred ligand. A slight variation of the above as in substrates **9**[8] and **11**[8] provides the [3.3.3]- and [3.3.4]propellanes **10**[8] and **12**[8] in 77 and 76% yields, respectively, at 50–55 °C. Further characterization of the [3.3.4]propellane involved hydrolysis (K$_2$CO$_3$, CH$_3$OH, room temperature), oxidation (PCC, CH$_2$Cl$_2$, room temperature), and olefin migration (DBU, CHCl$_3$, room temperature) to give the cyclopentenone **13**.



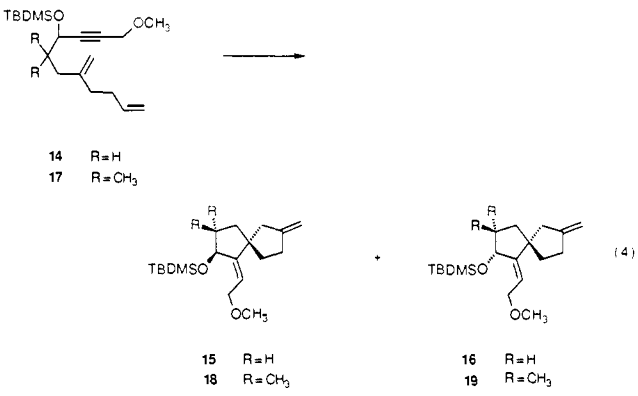
5 X = CE$_2$ **6** X = CE$_2$
7 X = NTs **8** X = NTs



9 n = 1, R = TBDMS **10** n = 1, R = TBDMS
11 n = 2, R = Ac **12** n = 2, R = Ac

13 n = 2

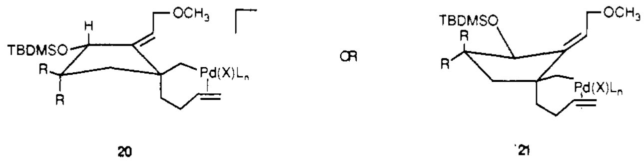
Substrates bearing disubstituted acetylenes participate even better than those bearing terminal acetylenes (eq 4). Contrasting substrates **14**[8] and **17**[8] reveals that *gem* substitution is not required (86–88% yields), but such substitution does affect diastereoselectivity ([**15**]:[**16**],[8] 1:1.3; [**18**]:[**19**],[8] <1:>20).



14 R = H
17 R = CH$_3$

15 R = H **16** R = H
18 R = CH$_3$ **19** R = CH$_3$

All of the above results are consistent with the notion that a ligated hydridopalladium acetate, formed in situ by oxidative addition of Pd(0) with acetic acid, initiates cyclization by chemoselective addition to the acetylene.(9) The resultant vinylpalladium species undergoes intramolecular carbopalladation which, in the case of **14** and **17**, corresponds to **20** and **21**. When R = H, the transition states (ts) leading to these two intermediates should be similar in energy, thus producing **15** and **16** in nearly equal amounts. On the other hand, when R = CH$_3$, the severe 1,3-interaction between the methyl and pendant butenyl chain destabilizes the ts leading to **20** sufficiently that only **21** and consequently **19** forms.

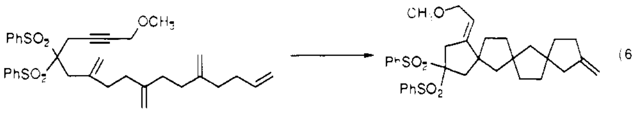


20 **21**

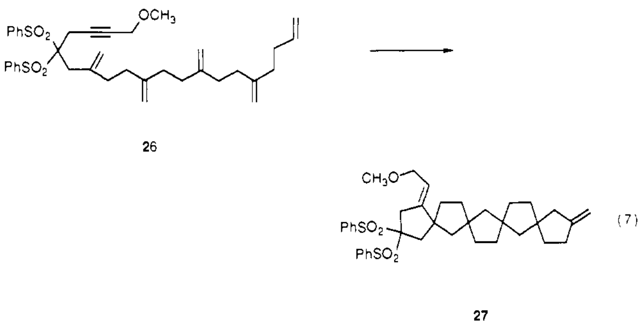
The fact that each cyclization forms a new C–Pd bond suggests that the presence of additional unsaturation should permit additional rings to form. Indeed, the trienyne **22**[8] cyclizes under our usual conditions at room temperature to the dispiro compound **23**[8] in 81% yield (eq 5)! The ^{13}C NMR spectrum indicates the product is a 7:1 diastereomeric mixture in which the major diastereomer is tentatively assigned as depicted based upon mechanistic considerations.

22 **23**

How many rings can be formed in one step? In order to examine this question and to probe the effect of employing a disubstituted acetylene as the initiator, we explored the cyclizations of **24**[8] (eq 6) and **26**[8] (eq 7). Incredibly, the tetra- and pentacycles **25**[8] and **27**[8] form in 84 and 86% yields, respectively, using 10 mol % triphenylstibine as the preferred ligand at 40–55 °C!



24 **25**



26

27

Conceptually, these reactions resemble a zipper in which the π-bonds are the teeth and the palladium is the tab. Pulling the tab across the teeth converts π-bonds to σ-bonds with creation of polycycles. This polyolefin cyclization does require, however, an acetylene initiator. The unusual polyspirocycles **25** and **27** constitute an interesting structural type with a novel helicity.(10) Remarkably, spectroscopic and chromatographic data suggest that, in spite of the fact that four and eight diastereomers, respectively, are possible, each is mainly a mixture of only two stereoisomers.

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Clearly, cycloisomerization is a powerful tool for construction of polycycles in which the nature of the polycycle depends only upon the juxtaposition of the unsaturation.

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Supplementary Material Available: Characterization data for **1–12**, **14–17**, **19**, and **22–27** (6 pages). Ordering information is given on any current masthead.

Nonlinear Optical and Excited-State Properties of Conjugated One-Dimensional $[N{\equiv}M(OR)_3]_n$ Polymers

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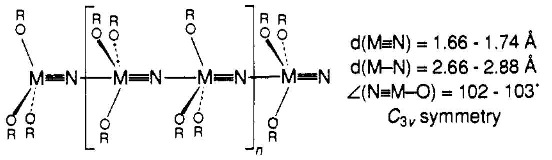
Conjugated organic molecules and polymers have long been the subjects of extensive study, in part because their delocalized π-electron systems endow these materials with enhanced electrical conductivities[1] and nonlinear optical[2] responses. We have been interested in the comparatively small and unexplored class of transition-metal complexes and polymers that are structurally and, in a formal sense, electronically analogous to such conjugated organic materials, on the basis of our expectation that the incorporation of optically tunable and redox-tunable unsaturated metal centers into conjugated structures should further augment their physical properties.[3] This has led us to investigate the class of one-dimensional polymers of the type $[N{\equiv}M(OR)_3]_n$ (M = Mo, W).[4,5] The structures of these[5] and related[6] metal–nitrido polymers differ from those typical of linear-chain transition-metal compounds[7] in that they display a distinct bond-length alternation along the polymer backbone; band-structure calculations[8] and qualitative bonding considerations suggest that these species may be viewed as analogues of hydrocarbon polyenes and polyynes. Herein we report that these metal–nitrido polymers represent a new class of highly optically transparent inorganic nonlinear-optical materials and that they possess unusual photophysical properties.[9]



Time-resolved spectroscopic analysis of the light emitted by powdered samples of $[MN(OR)_3]_n$ (M = Mo, R = CMe_3, CMe_2CF_3; M = W, R = CMe_3)[4,5b] upon irradiation with the 1064-nm output of a pulsed Nd:YAG laser reveals a line at the frequency-doubled wavelength of 532 nm whose width and temporal profile are comparable to those of the excitation pulse. The observation of this second-harmonic generation (SHG) for $[MoN(OCMe_3)_3]_n$ and $[WN(OCMe_3)_3]_n$ is consistent with the fact that they crystallize in noncentrosymmetric space groups ($P6_3cm$, $P6_3$),[5] thus fulfilling a prerequisite for possessing bulk second-order susceptibilities ($\chi^{(2)}$).[2c,10,11] In contrast, the compound $[MoN(OCMe_2Et)_3]_n$ displays no SHG signal. Given the

Table I. Photophysical and Second-Harmonic Generation Data for $[MN(OR)_3]_n$

polymer	SHG efficiency[a]	emission: $\bar{\nu}_{max}$ (fwhm),[b] cm^{-1} [c,d]	emission: τ, μs [c,e]
$[WN(OCMe_3)_3]_n$	0.20	19 490 (4980)	60
$[MoN(OCMe_3)_3]_n$	0.25	18 000 (4920)	750
$[MoN(OCMe_2CF_3)_3]_n$	0.35	18 890 (5160)	*f*
$[MoN(OCMe_2Et)_3]_n$	*g*	18 050 (4930)	760

[a] Efficiency (urea = 1) of unsized powders (λ_{ex} = 1064 nm). [b] Fwhm = full width at half maximum. [c] Crystalline sample, T = 77 K. [d] Corrected for spectrometer response. [e] λ_{ex} = 266 nm (Nd:YAG fourth harmonic, 5-ns fwhm pulse width, power < 100 μJ/pulse). Single-exponential emission decays were observed over at least five emission lifetimes. [f] Reproducible and single-exponential emission decays were not observed due to photodecomposition. [g] No signal observed.

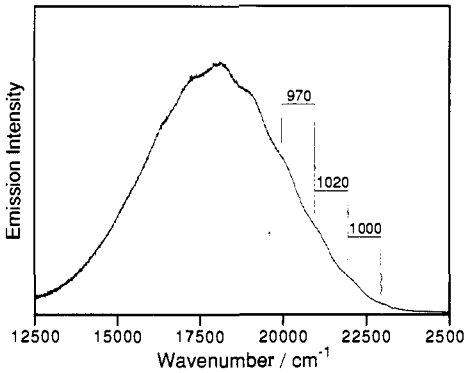


Figure 1. Emission spectrum (corrected for spectrometer response) of crystalline $[MoN(OCMe_2Et)_3]_n$ at 77 K. Spacings (±50 cm^{-1}) of the ν(Mo≡N) vibronic progression are indicated.

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