The syn complexes 3 and 6 have a M–M bond in the unoxidized form, therefore requiring donation of only 6 π electrons from the bridging polyolefin to achieve the 18-electron configuration for each metal. When these complexes are oxidized, the ultimate products once again have two 18-electron metals (4 and 5 from 3, 7 from 6). In these cases, however, expansion of hapticity of the bridging polyolefin occurs through *loss of hydrogen* (as an atom or ion) from one of the polyolefin carbons. This is very similar to the hapticity expansions observed in mass spectrometry of metal π complexes.[34,35]

The one-electron intermediates 3^+ and 6^+ display considerably higher thermodynamic and kinetic stabilities than do the corresponding monocations of the anti complexes 11^+ and 1^+. This is not surprising, in view of the need to break relatively strong C–H bonds in 3^+ or 6^+ to produce the ultimate electrolysis products.

Conclusions

The *syn*-dirhodium complexes 3 and 6 oxidize in two discrete one-electron steps, in contrast to the case for the anti-dinuclear complex 11. This difference in behavior arises from greater stability of the one-electron intermediates in the oxidation of the syn complexes, owing to relatively slow cleavage of polyolefin C–H bonds in the radical cations. One-electron processes have also been reported for syn-dinuclear complexes of Cr and V,[36] therefore appearing to be the favored route for complexes in which a bonded pair of metals is coordinated to the same face of a polyolefin. The two-electron reactions noted for 11 and 1 require structural changes which are fast and reversible on the voltammetric time scale, involving at least in part significant changes in the degree of the metal–metal interaction. Such a change is not available to the *syn*-dirhodium complexes upon oxidation.

Acknowledgment. This work was generously supported by the National Science Foundation (Grant No. CHE 86-03728). We are also grateful to the Johnson Matthey Co. for a loan of rhodium trichloride and to Dr. Albrecht Salzer for a sample of $Cp_2Rh_2(\eta^6\text{-}C_8H_8)$.

Supplementary Material Available: Ambient-temperature ^1H and $^{13}C\{^1H\}$ NMR spectra of 7 in DMSO-d_6 (1 page). Ordering information is given on any current masthead page.

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[34] Litzow, M. R.; Spaulding, T. R. *Mass Spectrometry of Inorganic and Organometallic Compounds*; Elsevier: Amsterdam, 1973; Chapter 11, Section 8–12.

[35] For example, $[Cp^*Rh(\eta^4\text{-}C_5Me_5H)]^+ \rightarrow Cp^*_2Rh^+$: Cloke, F. G. N.; Day, J. P.; Greenway, A. M.; Seddon, K. R.; Shimran, A. A.; Swain, A. C. *J. Organomet. Chem.* **1989**, *372*, 231.

[36] Bachman, B.; Han, F.; Heck, J.; Wuensch, M. *Organometallics* **1989**, *8*, 2523.

Transition-Metal-Promoted Conversion of Dichlorovinylcyclobutanes to Cyclohexadienes

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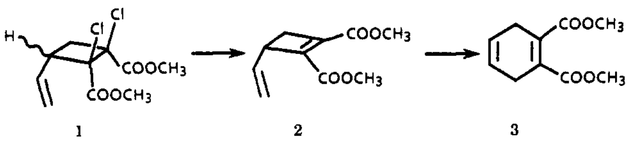
The nickel(0)- and iron(0)-promoted dechlorination of dimethyl 1,2-dichloro-3-vinylcyclobutane-1,2-dicarboxylate (1) to dimethyl 3-vinylcyclobutene-1,2-dicarboxylate (2) occurs faster in the trans isomer. Nickel(0) and nickel(I), but not iron(0), with promote the rearrangement of this vinylcyclobutene to dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate (3). The effect of methyl substituents on these reactions indicate that the nickel must transfer to the vinyl group before the rearrangement can occur. It also was found that nickel will cleave exclusively the bond between an sp^2- and an sp^3-hybridized carbon.

A number of years ago, we reported[1a,2] that the $Ni(CO)_4$-promoted dechlorination and ring expansion of dimethyl 1,2-dichloro-3-vinylcyclobutane-1,2-dicarboxylate (1) to dimethyl 1,4-cyclohexadiene-1,2-dicarboxylate (3) occur in two distinct steps with dimethyl 3-vinylcyclobutene-1,2-dicarboxylate (2) as an isolable intermediate.



1 2 3

In addition, we showed by deuterium labeling experiments that this reaction is unimolecular, and it is an sp^2 and not an sp^3 carbon of vinylcyclobutene (2) which migrates to give the product. This reaction represents one of only a few cases in which an sp^2 carbon rather than an sp^3 carbon undergoes a metal-promoted migration.[3]

More recently,[1b] we showed that the transformation of 2 to 3 could be promoted by $(PPh_3)_2Ni(C_2H_4)$ at elevated temperatures, or by $(PPh_3)_2Ni(C_2H_4)$ at room temperature if the nickel(0) is first oxidized to nickel(I). We speculated that the role of the oxidation was to allow transfer of the nickel from the ring double bond to the vinyl group. In this paper, the effect methyl substituents have on this unique isomerization reaction will be studied in order to

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[1] (a) DiFrancesco, D.; Pinhas, A. R. *J. Org. Chem.* **1986**, *51*, 2098. (b) Choi, H.; Hershberger, J. W.; Pinhas, A. R.; Ho, D. M. *Organometallics* **1991**, *10*, 2930.

[2] Also see: Scharf, H.-D.; Korte, F. *Chem. Ber.* **1966**, *99*, 1299, 3925.

[3] See for example: (a) Hughes, R. P.; Robinson, D. J. *Organometallics* **1989**, *8*, 1015 and references cited therein. (b) Grabowski, N. A.; Hughes, R. P.; Jaynes, B. S.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1986**, 1694.

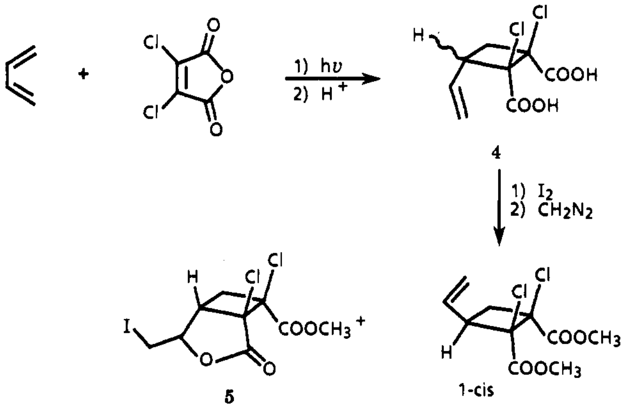
determine if the metal must interact with the vinyl group before the ring expansion reaction can occur. However, first, a closer examination of the dechlorination reaction will be taken.

Results and Discussion

Dechlorination of Compound 1. Becuase the synthesis of compound 1 generates about a 50/50 mixture of two stereoisomers, we were interested to determine if one of the isomers dechlorinates faster than the other, as previously suggested.[2] Monitoring the $Ni(CO)_4$-promoted dechlorination reaction by gas chromatography readily showed that the 19.9-min peak in the GC trace of the starting material converts to compound 2 about 3 times faster than the 20.6-min peak, and thus, one isomer of the starting vinylcyclobutane does react faster than the other isomer.

Unfortunately, the standard chromatographic techniques of TLC, column chromatography, HPLC, and preparative GC did not allow us to separate these two isomers. In addition, although decoupling experiments of the ^1H NMR spectrum give the assignment of which resonances belong to one compound and which belong to the other, there is not enough difference in these two NMR spectra to allow positive identification of which spectrum belongs to the cis isomer and which belongs to the trans. However, positively determining which peak in the GC trace is which isomer was accomplished by making the iodolactone derivative.

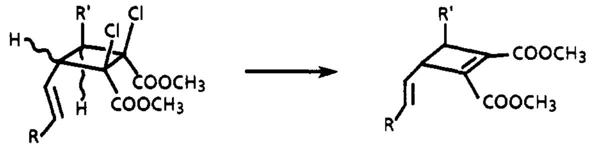
After the standard photocyclization and hydrolysis reactions, the mixture of isomeric acids (4) was subjected to iodine in acetonitrile at room temperature.[4] This mixture was then esterified with diazomethane. The iodine has no effect on the isomer in which the carboxylic acids are trans to the vinyl (4-*cis*), but converts the isomer in which they are cis (4-*trans*) into an iodolactone. Injecting this mixture into the gas chromatograph shows the 20.6-min peak of the original mixture of esters is still present, the 19.9-min peak has greatly decreased in size, and a longer retention time peak (35.4 min) accounts for the "missing" material in the 19.9-min peak. Thus, the 20.6-min peak in the gas chromatograph corresponds to the cis isomer (1-*cis*), and the 19.9-min/peak corresponds to the trans isomer. Therefore, the isomer 1-*trans* dechlorinates faster than the isomer 1-*cis*.



At this time, compound 1 was treated with a number of other readily available metal sources to determine the ability of each to effect this dechlorination reaction. Compound 1 did not react with $Cr(CO)_6$ even in refluxing benzene. The use of $Fe(CO)_5$ or $Co_2(CO)_8$ gives a mixture which includes cyclobutene 2, cyclohexadiene 3, and large amounts of many other compounds.[5] On the other hand, $Fe_2(CO)_9$ dechlorinates 1 at room temperature in either benzene or THF. Unfortunately, the dechlorination of 1 with $Fe_2(CO)_9$ needs an extended period of time and gives a low yield (23%). As with $Ni(CO)_4$, the trans isomer dechlorinates about 3 times faster than the cis isomer.

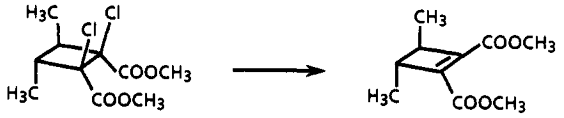
Compound 1 is most easily dechlorinated with another nickel(0) complex, $(PPh_3)_2Ni(C_2H_4)$,[6] in about 15 min at room temperature in THF. The yield of this reaction is 40–45%. Due to the fast rate of this reaction, it cannot be directly determined which isomer of 1 dechlorinates more rapidly. However, when a deficiency of $(PPh_3)_2Ni(C_2H_4)$ is used, the unreacted starting material is always 1-*cis*.

The exact reason(s) for this difference in rate is not known, but it may be simply a steric problem. Consistent with this idea is the observation that the dechlorination of 6 proceeds 1.5–2 times more quickly than does the dechlorination of 7.



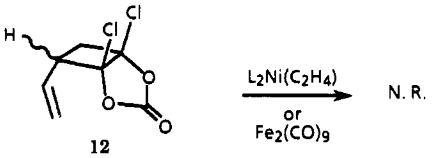
6 R = CH_3 R' = H 8
7 R = H R' = CH_3 9

Alternatively, the metal may initially coordinate to the vinyl group and then be delivered to the backside of the carbon–chlorine bond. However, this idea seems unlikely based on the observation that cyclobutene 11 which does not contain a vinyl group also can be obtained from its dichloride.[2]



10 11

To study whether the ester groups are required for this dechlorination reaction, dichloride 12 was synthesized.[7,8] Upon treatment with either $(PPh_3)_2Ni(C_2H_4)$ or $Fe_2(CO)_9$, compound 12 was recovered unchanged; and thus, the metal cannot promote the dechlorination of a dichloride when the chlorine bearing carbons are electron rich.



12

Isomerization of 2 to 3 with $Ni(CO)_4$. As stated above, previously it was shown that the isomerization of

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(4) (a) Bartlett, P. A.; Myerson, J. *J. Am. Chem. Soc.* **1978**, *100*, 3950. (b) Barnett, W. E.; Sohn, W. H. *Tetrahedron Lett.* **1972**, 1777. (c) Ranganathan, S.; Raganathan, D.; Mehrotra, A. K. *Tetrahedron* **1977**, *33*, 807.

(5) DiFrancesco, D. M.S. Thesis, University of Cincinnati, Cincinnati, OH, 1988.

(6) $(PPh_3)_2Ni(C_2H_4)$ was synthesized according to: (a) Ashley-Smith, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc. A* **1969**, 3019. (b) Wilke, G.; Herrmann, G. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 549.

(7) (a) Scharf, H.-D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 520. (b) Scharf, H.-D.; Seidler, H. *Ibid.* **1970**, *9*, 900. (c) Scharf, H.-D.; Droste, W.; Liebig, R. *Ibid.* **1968**, *7*, 215.

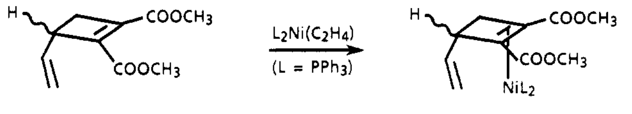
(8) (a) Scharf, H.-D.; Pinske, W.; Feilen, M.-H.; Droste, W. *Chem. Ber.* **1972**, *105*, 554. (b) Ellingboe, E. K.; Melby, L. R. U.S. Patent 2816287, 1957.

2 to 3 is a unimolecular reaction.[1a] Because we were interested to learn what intermediate metal complexes are involved in this transformation, the reaction of 2 with $Ni(CO)_4$ was monitored by ^1H NMR spectroscopy. Although this reaction is usually run in refluxing benzene (bp = 80 °C), for safety reasons, the probe of the NMR spectrometer could be taken to only 55 °C. This spectrum reveals the presence of only compound 2; no new peaks which could be assigned to an intermediate metal complex or to product 3 were observed.

The trapping of an organometallic intermediate by a small molecule, to form a ring larger then six-membered or some other new organic compound, also was attempted. When carbon dioxide, dimethyl acetylenedicarboxylate, dimethyl maleate, styrene, or norbornene (large excess) was added to a mixture of 2 and $Ni(CO)_4$, the only organic compound observed was 3.

Attempted Isomerization of 2 to 3 with $Fe_2(CO)_9$. Although the dechlorination reaction readily goes in the presence of $Fe_2(CO)_9$, the isomerization reaction of 2 to 3 does not. Vinylcyclobutene 2 can be stirred in the presence of a large excess of $Fe_2(CO)_9$ for 2 days and still no trace of 3 is observed by gas chromatography. This result is very different from the Fe(0)-promoted ring expansion of a vinylcyclopropene to the η^4-cyclohexa-2,4-dienone complex.[3] In that reaction, $Fe_2(CO)_9$ reacts smoothly with 1,2,3-triphenyl-3-vinylcycloprop-1-ene at room temperature to give the ring-expanded product. At this time it is unknown why Fe(0) will react with the vinylcyclopropene but not with the vinylcyclobutene.

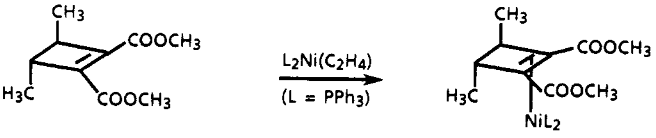
Isomerization of 2 to 3 with $(PPh_3)_2Ni(C_2H_4)$. As shown previously,[1b] the reaction between 2 and $(PPh_3)_2Ni(C_2H_4)$ generates a 50/50 mixutre of complexes 13-*syn* and 13-*anti*.



2 13

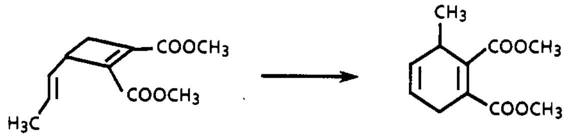
Complex 13 is stable for an extended period of time if kept at room temperature under an inert atmosphere. However, upon being heated in refluxing benzene or THF under an inert atmosphere, nickel complex 13 rearranges to cyclohexadiene 3. The conversion of 13 to 3 will occur at room temperature if the nickel(0) is oxidized to nickel(I). Though a variety of chemical oxidants (such as Cp_2Fe^+ and L_2NiBr_2) can be used, this transformation is most easily accomplished by exposure of the reaction mixture to air.[1b] When this rearrangement reaction is monitored by ^1H NMR spectroscopy, no intermediate metallacyclic complexes can be observed. This result, together with the $Ni(CO)_4$ monitoring and trapping studies, suggests that the initial bond breaking step is rate determining and all subsequent steps are very fast.

When $(PPh_3)_2Ni(C_2H_4)$ was allowed to react with cyclobutene 11, complex 14 is formed. The ester carbonyl stretches in the IR spectrum and the resonances due to the olefinic carbons in the ^{13}C NMR spectrum 14 are very similar to those observed for complex 13. However, consistent with our previous suggestion of nickel cleaving only an sp^2–sp^3-hybridized bond, upon exposure to air, 14 converts back to 11; no 2,4-hexadiene derivative was observed.



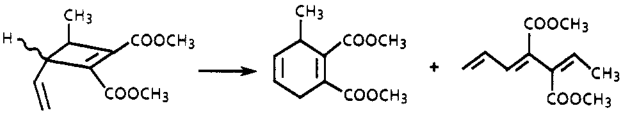
11 14

Isomerization of Monomethyl Analogues of 1. Because no complex other than 13 could be observed spectroscopically and because no intermediate complex could be trapped in these reactions, we wanted to determine if the vinyl group was involved in this isomerization reaction, as it is in the ruthenium-promoted ring expansion of a vinylcyclopropene.[3] This study was accomplished by using vinylcyclobutene 8 in which the vinyl group is substituted by a methyl. The reaction of vinylcyclobutene 8 with $Ni(CO)_4$ generates exclusively the cyclohexadiene derivative 15. (The authenticity of cyclohexadiene 15 was ensured by an independent synthesis using a Diels–Alder reaction of *trans*-1,3-pentadiene and dimethyl acetylenedicarboxylate.) This reaction proceeds about 5 times more *slowly* than the analogous conversion of 2 to 3. Thus, the effect a methyl substituent on the vinyl group has on the rate of this reaction is similar to that observed for the ruthenium-promoted ring expansion reaction mentioned above.[3] The starting vinylcyclobutene 8 was recovered unchanged upon treatment with $(PPh_3)_2Ni(C_2H_4)$ followed by an air oxidation.



8 15

Because it was obtained as a side product in the synthesis of compound 8, the reactivity of vinylcyclobutene 9 in which the ring is substituted with a methyl group was studied; however, this isomer could not be obtained free of 8. A mixture of these two methyl-substituted compounds was subjected to $Ni(CO)_4$ in refluxing benzene to yield cyclohexadiene derivative 15 and a small amount of dimethyl 1,3,5-heptatriene-4,5-dicarboxylate. (The heptatriene most likely comes from a thermal reaction; see below.)

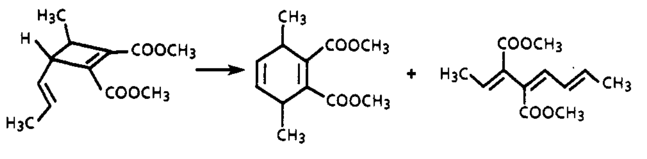


9 15 16

A mixture of the two methyl-substituted isomers also was subjected to the standard $(PPh_3)_2Ni(C_2H_4)$ reaction conditions (THF, room temperature) to yield unreacted vinylcyclobutene 8 and cyclohexadiene 15.

Isomerization of a Dimethyl Analogue of 1. When the dimethyl analogue of 2 (18) was treated with $Ni(CO)_4$, both *cis*-3,6-dimethyl- and *trans*-3,6-dimethyl-1,4-cyclohexadiene-1,2-dicarboxylate (19) are formed in about a 2/1 ratio. However, these two compounds represent only a minor component of the product mixture; the product mainly is a mixture of octatrienes (20). The octatrienes were unexpected because they are formed by the breaking an sp^3–sp^3-hybridized bond.

On the basis of results with monomethyl compounds 8 and 9, it was anticipated that 18 would not react with $(PPh_3)_2Ni(C_2H_4)$; and as expected, upon treatment with $(PPh_3)_2Ni(C_2H_4)$, the two cyclohexadienes are formed in less than 1% as determined by gas chromatography. However, the final organic product is not unreacted vinylcyclobutene 18, but rather, it is exclusively an isomeric mixture of octatrienes 20.



18 19 20

It was determined that, in the above reactions, formation of **20** is not a metal-promoted process. When compound **18** is allowed to stir overnight at room temperature *in the absence of any metal source*, the same mixture of octatrienes is formed. Thus, the trans arrangement of the methyl and the vinyl on the ring must facilitate the thermal breaking of the C3–C4 bond. This result is most likely due to the smaller bond dissociation energy between a secondary carbon and a vinyl-substituted carbon as compared with a primary carbon and a vinyl-substituted one. The effect of substituents on this type of ring-opening reaction previously has been observed for the thermal (175 °C) conversion of *trans*-3,4-dimethylcyclobutene to hexadiene as compared with the conversion of cyclobutene to butadiene.[9]

Conclusion

Our results show that with $Ni(CO)_4$ the methyl substituent on the vinyl group decreases the rate of the ring-expansion reaction. A direct observation of this point is the 5 times slower rate of conversion of **8** to **15** as compared with **2** to **3**. An indirect observation of this point, if one makes the assumption that vinylcyclobutenes **9** and **18** have equal facility for the thermal ring opening (to a triene) because they both have a vinyl group on C3 and a methyl on C4, is that compound **9** (with its methyl group only on the ring) undergoes mainly the metal-promoted ring-expansion reaction and compound **18** (with a methyl group both on the ring and on the vinyl group) undergoes mainly the thermal ring-opening reaction. When the much larger complex $(PPh_3)_2Ni(C_2H_4)$ is used as the metal source (followed by the required air oxidation), a methyl on the vinyl group (**8** and **18**) virtually stops the ring-expansion reaction. These results strongly suggest that although no intermediate could be observed or trapped, at some point the vinyl group must interact with the metal in the ring-expansion reaction. In addition, our results show that the nickel cleaves exclusively the bond between an sp^2- and an sp^3-hybridized carbon and that any breaking of an sp^3–sp^3-hybridized bond is due to a thermal reaction.

Experimental Section

General Procedures. All reactions were carried out with oven-dried glassware, under an argon atmosphere or in a drybox, using freshly distilled solvents. Gas chromatography conditions, mass spectral conditions, and the synthesis and complete characterization for compounds **1**–**3** were reported previously.[1]

All IR spectra were recorded on a Perkin-Elmer Model 599 infrared or a 1600 Series FTIR spectrophotometer using KBr cells. All NMR spectra were recorded on a Nicolet NT-300 or a Bruker 250-MHz spectrometer and referenced to TMS at 0.00 ppm.

HPLC separations were performed using a Kratos high-pressure liquid chromatograph with a Kratos Spectroflow 783 detector, two Spectroflow 400 pumps, a Spectroflow 591 static mixture/injector, a 250 × 7.0 mm reversed-phase C_{18} column, gradient programming, and a 1 mL/min flow rate. The solvents were deaerated HPLC-grade CH_3CN and H_2O filtered with the Nanopure II system. Preparative TLC was performed using silica gel plates and eluting with 15% ethyl acetate in petroleum ether.

Iodolactonization of 1,2-Dichloro-3-vinylcyclobutane-1,2-dicarboxylic Acid Followed by Esterification. To 0.30 g (1.3 mmol) of a mixture of the cis and trans carboxylic acids (these were synthesized as discussed in ref 1) in 10 mL of acetonitrile at 0 °C was added dropwise 0.32 g (1.3 mmol) of I_2 in 13 mL of acetontrile. This reaction was allowed to warm to room temperature and then to stir overnight. The solution was acidified with 10% HCl, saturated with NaCl, and then extracted with 30 mL of ether. The ether layer was washed with a saturated sodium bisulfite solution until the water layer was clear and was dried with magnesium sulfate. The ether was removed, and the mixture of diacid and iodolactone was esterified with diazomethane as described previously. MS of product, *m/e*: 343 (48%), 258 (21%), 148 (28%), 141 (27%), 127 (32%), 113 (30%), 77 (67%), 59 (100%).

Dechlorination of 1 with $Fe_2(CO)_9$. The isomeric mixture of **1** (1.00 g, 3.75 mmol) was dissolved in 30 mL of benzene. This solution was degassed with argon for 10 min, and then 2.73 g (7.50 mmol) of $Fe_2(CO)_9$ was added to the solution. This mixture was allowed to stir at room temperature for 48 h. An additional 2 equiv of $Fe_2(CO)_9$ was added to the mixture during this period (1 equiv each time). The reaction mixture was filtered, the benzene was then removed in vacuo, and the resulting crude product was dissolved in 50 mL of acetone. $FeCl_3$ was added to this solution until the bubbling stopped. Following this, 50 mL of ether was added, and the ether layer was washed with saturated sodium bisulfite until the water layer was clear and was dried with potassium carbonate. After removal of the solvent, a yellow oil was obtained (23% yield) which by gas chromatography and GC/MS contains 16% **1**, 60% **2**, and 24% of a dimer of **2**. MS for the dimer, *m/e*: 392 (21%), 361 (33%), 301 (31%), 269 (71%), 196 (100%), 165 (15%), 137 (24%). Compound **3** has never been observed from this reaction.

When this reaction is monitored by gas chromatography, the 19.9-min peak in the GC trace disappears about 3 times faster than the 20.6-min peak.

Dechlorination of 1 with $Co_2(CO)_8$. The isomeric mixture of **1** (0.10 g, 0.38 mmol) was dissolved in benzene (5 mL). This solution was degassed with argon for 7 min, and then $Co_2(CO)_8$ (0.26 g, 0.75 mmol) was added. This mixture was allowed to stir at room temperature for 2 days. An additional 1 equiv of $Co_2(CO)_8$ was added every 12 h. Results are as follows: 27% of **1** does not react, 33% converts to **2**, and 40% of **1** generates the dimers of **2** as determined by gas chromatography and GC/MS.

Dechlorination of 1 with $(PPh_3)_2Ni(C_2H_4)$. To the isomeric mixture of **1** (0.25 g, 0.94 mmol) dissolved in degassed THF (60 mL) was added, in the drybox, $(PPh_3)_2Ni(C_2H_4)$ (0.74 g, 1.2 mmol).[6] Typically, the reaction was allowed to stir at room temperature for 1 h. The mixture was then removed from the drybox and exposed to air, and the solvent was removed by vacuum distillation. The 2–3 mL of hexane was added to the residue. The solid which formed was filtered, and the hexane solution was concentrated. Following this, THF (2 mL) and methyl iodide (0.60 g, 4.2 mmol) were added and the mixture was allowed to stir at room temperature for 30 min. The white precipitate ($Ph_3PCH_3^+I^-$) was filtered. After the solvent was removed from the filtrate, the residue was purified using a short Florisil column, eluting with 33% THF in hexane. A pale yellow oil for compound **2** was obtained (0.08 g, 0.4 mmol, 40% yield).

Attempted Trapping of Organometallic Intermediates. To 3 mL of benzene were added 0.05 g (0.3 mmol) of **2**, 0.033 mL (0.26 mmol) of dimethyl acetylenedicarboxylate, 0.12 mL of dimethylformamide, and 0.20 mL (1.6 mmol) of $Ni(CO)_4$. This mixture was allowed to reflux for 2 h. After a workup with iodine, the products are **3** and, tentatively, hexamethyl benzenehexacarboxylate. ^1H NMR ($CDCl_3$), δ: 3.88 (s).

In a similar manner, **2** was treated with dimethyl maleate (0.32 mL, 0.26 mmol), styrene (0.30 mL, 0.26 mmol), excess norbornene (0.12 g, 1.27 mmol), or excess carbon dioxide. In each case, after workup, compound **3** was the only product observed by gas chromatography and ^1H NMR spectroscopy.

Preparation of 6. Into a thick-walled phototube were added *trans*-1,3-pentadiene (1.00 g, 14.7 mmol), dichloromaleic anhydride (2.45 g, 14.7 mmol), benzophenone (0.17 g, 0.90 mmol), and dioxane (26 mL). The reaction mixture was photolyzed, hydrolyzed, and esterified in the usual manner[1] to give a crude isomeric mixture of compounds. After Kugelrohr distillation (1.07 g, 3.81 mmol, 26% yield), compound **6** was isolated from the mixture by HPLC.

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[9] Winter, R. E. K. *Tetrahedron Lett.* **1965**, 1207.

(Compound **6** was contaminated by a small amount of the ring-substituted regioisomer **7**; the ratio of two compounds is about 5/1.) ^{1}H NMR of the HPLC-separated mixture of two isomers (CDCl$_3$), δ: 1.25 (d, J = 6.6 Hz, 0.6 H, due to minor isomer), 1.73 (d, J = 5.4 Hz, 3 H), 2.46 (dd, J = 10.5, 11.7 Hz, 1 H), 2.91 (dd, J = 8.1, 11.7 Hz, 1 H), 3.63–3.69 (m, 1 H), 3.77 (s, 1.2 H), 3.79 (s, 3 H), 3.81 (s, 3 H), 5.56–5.67 (m, 2 H). ^{13}C NMR (CDCl$_3$), δ: 17.9, 38.4, 41.8, 53.3, 53.8, 67.9, 76.1, 127.2, 130.4, 168.6, 169.2. IR (neat): 3006 (w), 2956 (m), 2853 (w), 1755 (s), 1731 (s), 1692 (w), 1641 (w), 1437 (s), 1282 (s) cm^{-1}. MS, *m/e*: 253 (0.3%), 251 (2%), 249 (3%), 247 (6%), 245 (16%), 215 (8%), 213 (23%), 185 (11%), 181 (12%), 153 (10%), 149 (6%), 125 (13%), 119 (12%), 91 (47%), 89 (17%), 59 (100%).

Dechlorination and Isomerization of 6 and 7. Compound **8**, which was prepared by the dechlorination of **6** using (PPh$_3$)$_2$Ni(C$_2$H$_4$) as discussed above, was treated with Ni(CO)$_4$ in the usual manner. After the workup, monomethylcyclohexadiene **15** was obtained. Compound **8** also was treated with (PPh$_3$)$_2$Ni(C$_2$H$_4$). After the usual oxidative workup, only starting material **8** was recovered.

^{1}H NMR of **8** (CDCl$_3$), δ: 1.67 (d, J = 5.7 Hz, 3 H), 2.41 (dd, J = 1.8, 15.0 Hz, 1 H), 2.87 (dd, J = 4.5, 15.6 Hz, 1 H), 3.50–3.56 (m, 1 H), 3.77 (s, 3 H), 3.78 (s, 3 H), 5.49 (ddq, J = 1.2, 6.3, 14.4 Hz, 1 H), 5.56–5.67 (m, 1 H).

^{1}H NMR of **15** (CDCl$_3$), δ: 1.15 (d, J = 6.9 Hz, 3 H), 2.93 (dd, J = 2.1, 7.4 Hz, 1 H), 3.00 (dt, J = 2.1, 7.5 Hz, 1 H), 3.21 (qd, J = 2.4, 7.5 Hz, 1 H), 3.76 (s, 3 H), 3.80 (s, 3 H), 5.67–5.71 (m, 2 H). ^{13}C NMR of **15** (CDCl$_3$), δ: 21.1, 27.7, 33.0, 52.7, 121.9, 129.5, 130.0, 140.8, 168.3, 169.7. IR of **15** (neat): 2954 (m), 2877 (w), 1724 (vs), 1680 (m), 1640 (m), 1456 (m), 1436 (s), 1282 (s), 1248 (s) cm^{-1}. MS, *m/e* of **13**: 210 (0.1%), 178 (24%), 177 (9%), 163 (48%), 151 (22%), 119 (34%), 105 (34%), 91 (100%), 79 (13%), 77 (40%).

A mixture of compounds **6** and **7** in a ratio of 2/1 was treated with Ni(CO)$_4$. Into a three-necked flask were added these compounds (1.0 g, 0.36 mmol), benzene (15 mL), dimethylformamide (1.0 mL), and Ni(CO)$_4$ (2.0 mL). The reaction mixture was allowed to reflux for 7 h. After a workup using iodine, compound **15** along with 10% heptatriene **16** was present (0.07 g, 0.33 mmol, 92% yield).

^{1}H NMR of dimethyl *cis*, *trans*-1,3,5-heptatriene-4,5-dicarboxylate (**16**) (CDCl$_3$), δ: 2.20 (d, J = 7.2 Hz, 3 H), 3.70 (s, 3 H), 3.74 (s, 3 H), 5.49 (dd, J = 1.5, 10.5 Hz, 1 H), 5.66 (d, J = 17.1 Hz, 1 H), 6.16 (q, J = 7.2 Hz, 1 H), 6.52–6.61 (m, 1 H), 7.28–7.40 (m, 1 H). IR (THF): 2951 (s), 2940 (s), 2878 (s), 1727 (s), 1380 (w), 1319 (w), 1261 (w) cm^{-1}. MS, *m/e*: 210 (20%), 179 (7%), 163 (9%), 151 (14%), 147 (9%), 119 (42%), 107 (16%), 91 (100%).

The 2/1 mixture of the same compounds (1.0 g, 0.36 mmol), (PPh$_3$)$_2$Ni(C$_2$H$_4$) (0.98 g, 1.6 mmol), and THF (60 mL) were mixed in the drybox. The reaction mixture was allowed to stir at room temperature for 24 h. The reaction was worked up in a usual manner to give compounds **8** and **15** in the ratio of 1.3/1 along with trace amounts of heptatrienes (0.030 g, 0.14 mmol, 40% yield).

Preparation of 11. Into a thick-walled phototube were added dichloromaleic anhydride (3.57 g, 21.4 mmol), benzophenone (0.25 g, 1.4 mmol), and dioxane (37 mL). The dioxane solution was frozen in a dry ice–2-propanol bath, and *trans*-2-butene (2 mL, 20 mmol) was added into the phototube. The tube was sealed and allowed to warm to room temperature. The reaction mixture was photolyzed, hydrolyzed, and esterified in the usual manner[1] to give an isomeric mixture of dichloro compounds. After Kugelrohr distillation, a pale yellow oil was obtained (3.45 g, 12.8 mmol, 60% yield). ^{1}H NMR (CDCl$_3$), δ: 1.02 (d, J = 6.9 Hz, 3 H), 1.22 (d, J = 6.6 Hz, 3 H), 2.49 (dd, J = 6.9, 11.4 Hz, 1 H), 2.89 (dd, J = 6.6, 11.1 Hz, 1 H), 3.75 (s, 3 H), 3.82 (s, 3 H). ^{13}C NMR (CDCl$_3$), δ: 12.5, 14.4, 41.1, 47.8, 52.7, 53.3, 73.2, 74.4, 168.4, 169.0. In addition, the ^{1}H and ^{13}C NMR spectra contain many small peaks due to cis isomers. IR (neat): 2957 (m), 2932 (m), 2874 (w), 2846 (w), 1753 (vs), 1728 (s), 1452 (s), 1437 (s), 1382 (m), 1332 (m), 1279 (vs), 1239 (s), 1213 (s) cm^{-1}. MS, *m/e*: 272 (0.1%), 270 (0.3%), 268 (0.3%), 237 (3.0%), 235 (2.2%), 233 (6.3%), 201 (6.8%), 181 (6.2%), 173 (8.8%), 137 (12.6%), 136 (17.4%), 135 (35.1%), 134 (47.2%), 103 (15.4%), 102 (16.7%), 79 (33.2%), 77 (49.6%), 59 (100%).

Into a 100-mL round-bottom flask were added, in the drybox, the dichloro compounds (0.12 g, 0.45 mmol), THF (60 mL), and (PPh$_3$)$_2$Ni(C$_2$H$_4$) (0.33 g, 0.54 mmol). The mixture was allowed to stir for 2 h at room temperature. At the end of this period, the reaction was worked up in an usual manner. The residue was a mixture of **11**-*trans* and **11**-*cis* in a ratio of 4/1. ^{1}H NMR of **11**-*trans* (CDCl$_3$), δ: 1.26 (d, J = 6.9 Hz, 6 H), 2.49 (q, J = 6.9 Hz, 2 H), 3.79 (s, 6 H). ^{13}C NMR of **11**-*trans* (CDCl$_3$), δ: 16.0, 43.8, 51.7, 145.0, 161.9. ^{1}H NMR of **11**-*cis* (CDCl$_3$), δ: 1.16 (d, J = 7.2 Hz, 6 H), 3.06–3.12 (m, 2 H), 3.79 (s, 6 H). ^{13}C NMR of **11**-*cis* (CDCl$_3$), δ: 12.2, 38.5, 51.7, 145.8, 161.9. IR of mixture (neat): 2957 (s), 2928 (s), 2870 (m), 1739 (vs), 1720 (vs), 1641 (s), 1455 (s), 1436 (s), 1373 (m), 1337 (s), 1308 (vs), 1289 (vs), 1257 (vs), 1219 (vs) cm^{-1}. MS, *m/e*: 198 (3.3%), 167 (18.8%), 166 (57.4), 151 (13.7%), 139 (6.6%), 138 (4.6%), 110 (7.2%), 107 (24.0%), 106 (24.9%), 95 (19.6%), 79 (100%), 77 (70.0%), 59 (74.9%).

Monitoring the Reaction between 11 and (PPh$_3$)$_2$Ni(C$_2$H$_4$) To Generate 14. In benzene-d_6 (1 mL) were dissolved **11** (0.04 g, 0.2 mmol) and (PPh$_3$)$_2$Ni(C$_2$H$_4$) (0.12 g, 0.20 mmol). This mixture was monitored by ^{13}C NMR spectroscopy. ^{13}C NMR (C$_6$D$_6$), δ: 14.03, 18.37, 21.85, 38.64, 43.04, 43.60, 49.65, 50.08, 64.38 (d, J = 20.5 Hz), 66.02 (d, J = 20.5 Hz), 66.42 (d, J = 25.2 Hz), 171.82, 171.94, 173.37, plus a large number of aromatic resonances.

In THF (3 mL) were dissolved **11** (0.10 g, 0.50 mmol) and (PPh$_3$)$_2$Ni(C$_2$H$_4$) (0.46 g, 0.80 mmol). This mixture was allowed to stir for 24 h and was then monitored by IR spectroscopy: the carbonyl stretches shift from 1739 and 1720 cm^{-1} to 1698 cm^{-1}. Upon exposure of complex **14** to air, only compound **11** was obtained.

Preparation of Compound 12. Butadiene (1 mL, 10 mmol) was condensed into a thick-walled phototube at −78 °C, and 4,5-dichloro-1,3-dioxol-2-one[7] (1.78 g, 11.4 mmol) dissolved in acetone (20 mL) was added to the phototube. The reaction mixture was photolyzed for 7 days by a (Hanovia) 450-W, mercury arc lamp. At the end of this time, the solvent was removed by vacuum distillation. The resulting compound **12** was purified using a short alumina column and eluting with 15% THF in petroleum ether. A yellow oil was obtained (0.36 g, 1.7 mmol, 15% yield). ^{1}H NMR of two steroisomers in a ratio of 1/1 (CDCl$_3$), δ: 2.71 (dd, J = 8.4, 14.1 Hz, 1 H), 2.83 (dd, J = 8.4, 14.4 Hz, 1 H), 3.08 (dd, J = 11.1, 14.4 Hz, 1 H), 3.20 (dd, J = 9.3, 14.1 Hz, 1 H), 3.51–3.60 (m, 1 H), 3.66–3.74 (m, 1 H), 5.22 (d, J = 17.1 Hz, 1 H), 5.30 (d, J = 17.1 Hz, 1 H), 5.40 (d, J = 11.7 Hz, 1 H), 5.41 (d, J = 11.4 Hz, 1 H), 5.82–5.96 (m, 2 H). ^{13}C NMR (CDCl$_3$), δ: 41.6, 41.9, 49.7, 50.0, 97.6, 98.5, 101.1, 102.8, 120.4, 121.1, 128.9, 132.3, 149.2, 149.3. IR (neat): 3079 (w), 2927 (s), 1850 (vs), 1733 (w), 1716 (m), 1642 (m), 1558 (w), 1540 (w), 1442 (m), 1430 (m), 1374 (m) cm^{-1}. MS, *m/e*: 156 (0.1%), 154 (0.1%), 131 (2.0%), 129 (5.7%), 122 (3.4%), 103 (5.4%), 101 (19.5%), 91 (10.3%), 89 (38.8%), 65 (100%), 54 (7.0%).

Attempted Dechlorination of Compound 12. Into a 50-mL round-bottom flask were added compound **12** (0.05 g, 0.2 mmol), THF (30 mL), and (PPh$_3$)$_2$Ni(C$_2$H$_4$) (0.29 g, 0.48 mmol) in the drybox. The reaction mixture was allowed to stir for 24 h at room temperature. The reaction was then worked up in a usual manner. Compound **12** was recovered unchanged.

Compound **12** was also treated with nonacarbonyldiiron. Into a 25-mL three-necked flask were added compound **8** (0.05 g, 0.2 mmol), benzene (8 mL), and nonacarbonyldiiron (0.17 g, 0.48 mmol). The reaction mixture was allowed to stir for 48 h at room temperature. Additional nonacarbonyldiiron (0.17 g, 0.48 mmol) was added to the reaction mixture during this period. The reaction mixture was filtered, and the solvent was removed by vacuum distillation. Dichloro compound **12** was recovered, as determined by gas chromatography.

Formation of (Cyclobutene)nickel Complex 13. To **2** (0.05 g, 0.3 mmol) dissolved in degassed THF (10 mL) was added, in the drybox, (PPh$_3$)$_2$Ni(C$_2$H$_4$) (0.3 g, 0.5 mmol). The reaction was monitored by IR spectroscopy. As soon as **2** was treated with (PPh$_3$)$_2$Ni(C$_2$H$_4$), the carbonyl stretches (all strong in intensity) for **2** at 1740 and 1724 cm^{-1} shifted to 1701 cm^{-1} and did not change as long as the mixture was left in the drybox.

In addition, the formation of nickel complex **13** in benzene-d_6 was monitored by ^{1}H and ^{13}C NMR spectroscopy. By ^{1}H NMR spectroscopy, the two singlets (3.39 and 3.38 ppm) for the methyl esters split into two sets of singlets immediately after the nickel–ethylene complex is added. One set is at 3.15 and 3.11 ppm, and the other one is at 2.98 and 2.96 ppm. (These peaks have the same chemical shifts at both 80 and 300 MHz.) Besides, the internal olefinic hydrogen of the vinyl group (5.63–5.73 ppm) moves downfield by 0.5–0.8 ppm (6.15–6.25 and 6.45–6.55 ppm). A peak for free ethylene also can be observed at 5.25 ppm. ^{13}C NMR for **9** (C_6D_6), δ: 32.57, 33.97, 41.99, 44.40, 49.60, 50.01, 50.24, 58.99 (d, J = 20.6 Hz), 59.67 (d, J = 21.4 Hz), 66.24 (d, J = 25.6 Hz), 66.85 (d, J = 22.7 Hz), 112.67, 112.77, 129.13, 129.25, 134.29, 134.39, 134.73, 134.85, 134.96, 135.31, 135.65, 142.13, 144.81, 171.31, 172.66, 173.08.

Thermal Ring Expansion of 13. To **2** (0.10 g, 0.50 mmol) dissolved in THF (5 mL) was added $(PPh_3)_2Ni(C_2H_4)$ (0.34 g, 0.56 mmol). The mixture was allowed to reflux for 10.5 h. At the end of this period, iodine (0.14 g, 0.56 mmol) was added to remove the organic ligand from the metal. After 30 min, the reaction was worked up in an usual manner. Both cyclohexadiene **3** and vinylcyclobutene **2** were observed in a ratio of 1/1 by gas chromatography.

Nickel complex **13**, prepared in a well-capped NMR tube, was allowed to stand in an oil bath (76 °C) for 6 h, and the reaction occasionally was monitored by ^{1}H NMR spectroscopy during this period. A substantial amount of cyclohexadiene **3** was observed along with nickel complex **13** within 2 h, and the amount of **3** slowly increased. At the end of 6 h, about 50% of **13** converted to **3** based on the integration of methyl groups of **13** and **3**. Peaks for compounds other than **3** and **13** were not observed.

Synthesis of Authentic 15. Into a thick-walled phototube were added *trans*-1,3-pentadiene (0.2 mL, 2.75 mmol), dimethyl acetylenecarboxylate (0.34 mL, 2.75 mmol), and dioxane (4.8 mL). The reaction mixture was allowed to react at room temperature for 3 days. After Kugelrohr distillation, compound **15** remained. The spectral data are the same as those reported above.

Preparation of 17. Into a thick-walled phototube were added dichloromaleic anhydride (0.92 g, 5.5 mmol), *trans*,*trans*-2,4-hexadiene (0.63 mL, 5.5 mmol), benzophenone (0.07 g, 0.4 mmol), and dioxane (9.6 mL). The reaction mixture was photolyzed, hydrolyzed, and esterified in a manner similar to that used in the preparation of compound **1**.[1] After Kugelrohr distillation, a clear oil remained (0.42 g, 1.4 mmol, 26% yield). ^{1}H NMR mixture of isomers ($CDCl_3$), δ: 1.02 (d, J = 6.6 Hz, 18 H), 1.15 (d, J = 7.5 Hz, 3 H), 1.16 (d, J = 7.5 Hz, 3 H), 1.21 (d, J = 6.6 Hz, 9 H), 1.23 (d, J = 6.3 Hz, 3 H), 1.68 (d, J = 6.9 Hz, 9 H), 1.70–1.77 (m, 9 H), 1.73 (d, J = 6.0 Hz, 18 H), 2.60–2.78 (m, 7.2 H), 2.89 (d, J = 7.8 Hz, 1.6 H), 2.92 (d, J = 7.8 Hz, 2 H), 3.14–3.21 (m, 4.8 H), 3.33 (d, J = 6.9 Hz, 4.2 H), 3.37 (d, J = 7.5 Hz, 4.2 H), 3.75 (s, 30 H), 3.77 (s, 12 H), 3.78 (s, 10 H), 3.82 (s, 12 H), 3.84 (s, 8 H), 5.10 (ddq, J = 1.5, 7.5, 15.0 Hz, 1 H), 5.25 (ddq, J = 1.5, 7.5, 15.3 Hz, 3 H), 5.53 (ddq, J = 1.5, 6.9, 15.3 Hz, 7 H), 5.61–5.80 (m, 13 H). IR (neat): 2955 (m), 1754 (s), 1728 (s), 1692 (w), 1679 (w), 1436 (s), 1279 (s) cm^{-1}. MS, m/e: 263 (12%), 261 (34%), 259 (100%), 229 (25%), 227 (71%), 191 (75%), 163 (26%), 133 (70%), 105 (70%), 91 (62%).

Dechlorination and Isomerization of 17 with $Ni(CO)_4$. Into a 25-mL three-necked flask were added the mixture of isomers of compound **17** (0.10 g, 0.34 mmol), dimethylformamide (1.0 mL), benzene (8 mL), and $Ni(CO)_4$ (2.0 mL, 16 mmol). The reaction mixture was allowed to reflux for 6 h. After the mixture cooled to room temperature, 30–50 mL of ether was added. The ethereal solution was allowed to stir with iodine (3.92 g, 15.4 mmol) for 20–30 min. The ether layer was washed repeatedly with a saturated sodium bisulfite solution until the washing resulted in a clear aqueous layer. The solution was dried with potassium carbonate, and the solvent was removed—a 1/4.5 mixture of **19** and **20** remained (0.07 g, 0.31 mmol, 94% yield). There are two isomers of **19** with the ratio of **19**-*cis* to **19**-*trans* equal to 2/1. ^{1}H NMR of **19**-*cis* ($CDCl_3$), δ: 1.21 (d, J = 6.9 Hz, 6 H), 3.10–3.17 (m, 2 H), 3.78 (s, 6 H), 5.67 (d, J = 2.7 Hz, 2 H). ^{1}H NMR of **19**-*trans* ($CDCl_3$), δ: 1.09 (d, J = 6.6 Hz, 6 H), 3.19–3.25 (m, 2 H), 3.77 (s, 6 H), 5.59 (d, J = 1.2 Hz, 2 H).

There are two isomers of **20** in about a 1/1 ratio as determined by ^{1}H NMR spectroscopy. These compounds were isolated by preparative TLC. ^{1}H NMR of dimethyl *trans*,*cis*,*trans*-2,4,6-octatriene-3,4-dicarboxylate (**20a**) ($CDCl_3$), δ: 1.85 (d, J = 5.4 Hz, 3 H), 2.20 (d, J = 7.2 Hz, 3 H), 3.70 (s, 3 H), 3.72 (s, 3 H), 6.11–6.30 (m, 3 H), 7.30 (d, J = 10.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$), δ: 15.9, 18.9, 51.5, 51.9, 127.8, 128.5, 139.9, 141.1, 143.8, 166.9, 167.7. IR (neat): 3030 (m), 2995 (m), 2951 (s), 2915 (m), 2848 (m), 1714 (vs), 1638 (s), 1598 (m), 1435 (s), 1377 (m), 1346 (m) cm^{-1}. MS, m/e: 224 (18%), 193 (8%), 192 (17%), 177 (25%), 165 (13%), 164 (17%), 133 (49%), 132 (12%), 121 (17%), 119 (12%), 106 (12%), 105 (70%), 104 (14%), 103 (21%), 91 (50%), 79 (47%), 77 (66%), 65 (33%), 59 (100%). ^{1}H NMR of dimethyl *trans*,*trans*,*trans*-2,4,6-octatriene-3,4-dicarboxylate (**20b**) ($CDCl_3$), δ: 1.88 (dd, J = 1.5, 6.8 Hz, 3 H), 2.10 (d, J = 7.2 Hz, 3 H), 3.71 (s, 3 H), 3.72 (s, 3 H), 6.09 (dq, J = 7.2, 14.6 Hz, 1 H), 6.27 (q, J = 7.5 Hz, 1 H), 6.53 (d, J = 11.4 Hz, 1 H), 7.11 (tq, J = 1.5, 11.1 Hz, 1 H). ^{13}C NMR ($CDCl_3$), δ: 15.9, 18.8, 51.5, 51.6, 128.8, 139.8, 139.9, 141.6, 166.8, 167.0. IR (neat): 2990 (m), 2951 (s), 2931 (s), 2852 (m), 1725 (vs), 1637 (s), 1593 (m), 1435 (s), 1360 (s), 1345 (s), 1291 (m) cm^{-1}. MS, m/e: 224 (30%), 209 (5%), 193 (14%), 192 (20%), 177 (42%), 165 (17%), 164 (20%), 149 (15%), 133 (61%), 132 (15%), 121 (21%), 105 (85%), 91 (57%), 79 (49%), 77 (74%), 65 (30%), 59 (100%).

Dechlorination and Isomerization of 17 with $(PPh_3)_2Ni(C_2H_4)$. Into a 50-mL round-bottom flask were added the mixture of isomers of compound **17** (0.09 g, 0.3 mmol), THF (60 mL), and $(PPh_3)_2Ni(C_2H_4)$ (0.76 g, 1.2 mmol). The reaction mixture was allowed to stir for 24 h at room temperature in the drybox. At the end of this period, the reaction was worked up in a manner similar to that used in the dechlorination of compound **1** by $(PPh_3)_2Ni(C_2H_4)$. The residue was a 3.3/1 mixture of octatriene **20** and vinylcyclobutene **18** (0.03 g, 0.1 mmol, 40% yield) along with a trace of cyclohexadiene **19**. The octatrienes **20** were about a 1/1 mixture of two compounds. One of these compounds is the same as **20b** from above, and the other is new. ^{1}H NMR of *trans*,*trans*,*cis*-2,4,6-octatriene-3,4-dicarboxylate (**20c**) ($CDCl_3$), δ: 1.86 (dd, J = 1.2, 6.6 Hz, 3 H), 2.13 (d, J = 7.2 Hz, 3 H), 3.71 (s, 3 H), 3.73 (s, 3 H), 5.92–5.98 (m, 1 H), 6.32 (q, J = 7.5 Hz, 1 H), 6.88 (d, J = 12 Hz, 1 H), 6.98 (tq, J = 1.5, 10.2 Hz, 1 H). The isomers of **18** cannot be separated. ^{1}H NMR of **18** ($CDCl_3$), δ: 1.12 (d, J = 7.2 Hz, 3 H), 1.14 (d, J = 7.2 Hz, 1.5 H), 1.29 (d, J = 6.6 Hz, 3 H), 1.67–1.73 (m, 7.5 H), 2.69 (qd, J = 1.5, 6.6 Hz, 1 H), 3.0 (d, J = 8.4 Hz, 1 H), 3.17 (dd, J = 4.5, 7.2 Hz, 1.5 H), 3.24 (qd, J = 4.5, 7.2 Hz, 1.5 H), 3.790 (s, 4.5 H), 3.794 (s, 4.5 H), 3.800 (s, 3 H), 3.804 (s, 3 H), 5.38 (ddq, J = 1.5, 7.5, 15.6 Hz, 1.5 H), 5.46 (ddq, J = 1.5, 7.2, 15.3 Hz, 1 H), 5.58 (dq, J = 7.5, 15.6 Hz, 2.5 H).

Synthesis of Authentic 19-*cis*. Into a thick-walled phototube were added *trans*,*trans*-2,4-hexadiene (0.32 mL, 2.8 mmol), dimethyl acethylenedicarboxylate (0.39 g, 2.8 mmol), and dioxane (4.8 mL). The reaction mixture was allowed to stir at room temperature for 7 days. After Kugelrohr distillation, **19**-*cis* was obtained. ^{1}H NMR ($CDCl_3$), δ: 1.21 (d, J = 6.9 Hz, 6 H), 3.10–3.17 (m, 2 H), 3.78 (s, 6 H), 5.67 (d, J = 2.7 Hz, 2 H). ^{13}C NMR ($CDCl_3$), δ: 22.2, 32.8, 52.1, 128.3, 137.9, 168.5. IR (neat): 1722 (vs), 1675 (m), 1636 (s), 1278 (s), 1246 (s), 1195 (s) cm^{-1}. MS, m/e: 209 (3%), 193 (25%), 192 (33%), 177 (86%), 165 (35%), 164 (21%), 133 (31%), 121 (25%), 119 (40%), 106 (23%), 105 (83%), 91 (86%), 79 (33%), 77 (50%), 59 (100%).

Thermal Triene Formation from 18. To **10** (0.10 g, 0.34 mmol) dissolved in THF (30 mL) was added $(PPh_3)_2Ni(C_2H_4)$ (0.41 g, 0.68 mmol). This mixture was allowed to stir at room temperature for 1 h. After workup, a mixture of isomers of **18** was obtained, contaminated by about 18% **20**.

Compound **18** was dissolved in 5 mL of THF, and the resultant mixture was allowed to stir at room temperature overnight (without any metal complex present). After the solvent was removed, mainly **20** was present with a small amount of **18**.

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