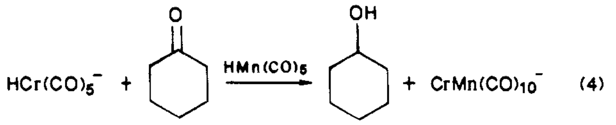
the catalyst recovery (Table I) as well as in situ studies. Nevertheless, the entry into μ-$HM_2(CO)_{10}^-$ catalysis (Scheme VI) is available from the acetate complex. Note that the major difference in reactivity of the μ-$HM_2(CO)_{10}^-$ and the $AcOM(CO)_5^-$ catalyst (or catalyst precursors) is in the case of M = Cr and substrate = cyclohexanone. This reduction has been shown to be difficult in the stoichiometric chemistry of $HCr(CO)_5^-$/acid/cyclohexanone.[1,2] In fact, the addition of ketone to $HCr(CO)_5^-$ does *not* occur in the absence of acid, and in Scheme V that event most probably occurs in reverse of the representation of Scheme V. That is the acetic acid is expected to serve as an acid promoter, activating the ketone functionality *prior* to hydride attack (as earlier represented in Scheme I).

Finally, the concept of group 6 metal pentacarbonyl complexes with Brønsted base ligands as catalyst precursors may be extended to less traditional bases. We have found the heterobimetallic anion, $MnCr(CO)_{10}^-$,[7] to be a catalyst (Table III, entry 23) for hydrogenation of cyclohexanone. A separate experiment demonstrated that the system $HCr(CO)_5^-/HMn(CO)_5$ could be used to reduce cyclohexanone to cyclohexanol (eq 5). Entry 23 shows the mixed metal dimer to be less efficient than the hydrido or acetato-metal pentacarbonyls as expected for the soft $Mn(CO)_5^-$ base having little configurational mobility for the simultaneous dissociation ($Mn^{\delta-}\cdots Cr$) and formation ($Mn^{\delta-}\cdots H^{\delta+}$) of bonds. Bases with more than one pair of unshared electrons more readily achieve transition states required in heterolytic cleavage.[5] These studies are continuing.



(4)

Acknowledgment. Support for this work was from the National Science Foundation, Grant No. CHE83-04162 (to M.Y.D.) and No. CHE83-08281 (to D.J.D.), and the Center for Energy and Mineral Resources of Texas A&M University. We are most grateful to Barnes Analytical (Spectra Tech Inc.) for the support of our research efforts.

Registry No. $W(CO)_5(OAc)^-\cdot PPN^+$, 36515-92-1; $Mo(CO)_5(OAc)^-\cdot PPN^+$, 76107-32-9; $Cr(CO)_5(OAc)^-\cdot PPN^+$, 99016-85-0; μ-$HW_2(CO)_{10}^-\cdot PPN^+$, 56172-01-1; μ-$HMo_2(CO)_{10}^-\cdot PPN^+$, 77214-68-7; μ-$HCr_2(CO)_{10}^-\cdot PPN^+$, 62341-83-7; PhCHO, 100-52-7; cyclohexanone, 108-94-1.

On the Mechanism of the Cyclooctatetraene Synthesis from Ethyne Employing Nickel Catalysts

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Abstract: The mechanism of the Reppe cyclization to cyclooctatetraene was investigated by employing ethyne-*1*-^{13}C as a substrate in the nickel-catalyzed reaction. The specific catalytic systems studied were nickel acetylacetonate–calcium carbide and nickel acetylacetonate–diethylaluminum ethoxide. In both cases, the label pattern in the cyclooctatetraene produced was consistent with either a stepwise coupling or concerted "zipper-type" mechanism of formation. These results preclude the possibility of cyclobutadiene or benzene intermediates or any carbon–carbon bond cleavage processes which do not leave the original connectivity in the alkyne intact. These conclusions were based upon analysis of the isotopic label in C_4 fragments, obtained by chemical degradation of the cyclooctatetraene produced.

The nickel-catalyzed cyclotetramerization of ethyne to cyclooctatetraene (COT) is a striking example of the capabilities of organometallic chemistry. Since its discovery by Reppe,[1] the reaction has been the subject of both synthetic and mechanistic inquiries.[3,4] While much information was garnered from these studies, there was little conclusive evidence to dismiss any of a variety of mechanisms postulated including a concerted process, stepwise growth at one or more nickel centers, or processes which contain either nickel–cyclobutadiene or nickel–benzene compounds as intermediates. It was our intent to try to distinguish among some of these possibilities using a labeling experiment. Preliminary results of this work have been published.[2]

For the purpose of discussion in this paper and in order for the reader to understand the motivation for our experiments, mechanistic alternatives have been grouped into four areas: concerted mechanisms, stepwise coupling sequences, mechanisms which feature symmetric intermediates such as cyclobutadiene or benzene, and those processes that may involve cleavage of the original alkyne triple bonds.

Concerted Mechanism. The simplest mechanism to envision is one in which the nickel atom acts as a template with all four ethyne molecules simultaneously bound to the metal prior to coupling (Scheme I). This view, espoused particularly by Schrauzer,[5] suggests that the critical intermediate, A, is an oc-

Scheme I

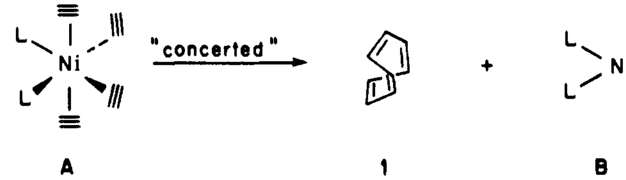

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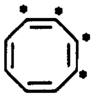
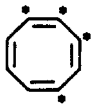
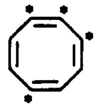
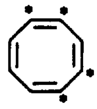
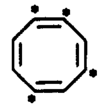
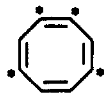
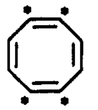
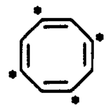
Table I. Theoretical Distribution (%) from Four Distinguishable Mechanisms

mechanism	scheme	 **1a**	 **1b**	 **1c**	 **1d**	 **1e**	 **1f**	 **1g**	 **1h**
stepwise or concerted	I, II	0.00	0.00	0.00	0.00	50.00	25.00	12.50	12.50
one symmetric intermediate	IV	0.00	6.25	6.25	6.25	43.75	18.75	6.25	12.50
cyclobutadiene dimerization	III	3.12	12.50	6.25	6.25	37.50	15.62	6.25	12.50
random		12.50	12.50	12.50	12.50	12.50	12.50	12.50	12.50

Scheme II

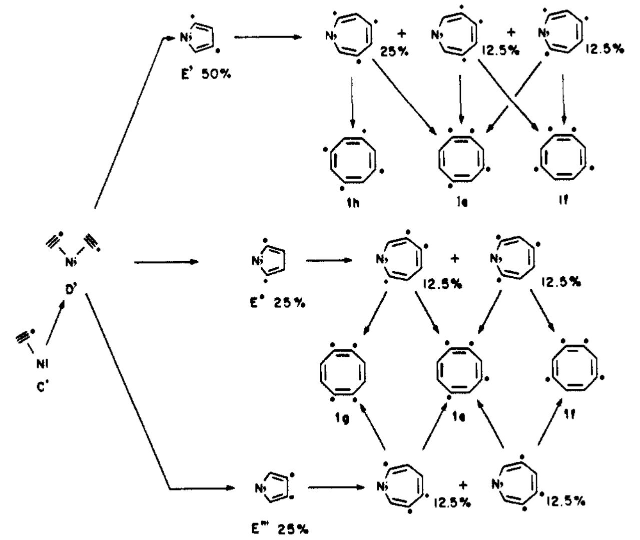


Figure 1.

tahedral complex in which the non-ethyne ligands occupy cis positions.[6,7]

Stepwise Mechanism. Another pathway which has perhaps achieved the greatest notoriety in recent years might be characterized by stepwise coupling. In this process each alkyne unit enters into the catalytic cycle in a distinct step. Scheme II is a schematic representation of a stepwise mechanism at a nickel center. Additional ligands have been omitted in the interest of clarity. Each kind of species in the scheme is well documented.[3,7-13] An elegant study by Whitesides and Ehmann[14] utilized a labeled butyne to show that most cyclotrimerization catalysts yielded products consistent with a stepwise mechanism. Recent developments in dinuclear chemistry have suggested that oligomerization may also take place in a stepwise fashion spanning two metal centers.[11,17-27]

Yet another type of stepwise mechanism features a metal hydride as the key species responsible for chain growth of oligomers.[28] Precedence exists for acetylide hydride intermediates in both catalytic[29,31] and stoichiometric[30] reactions with alkynes.

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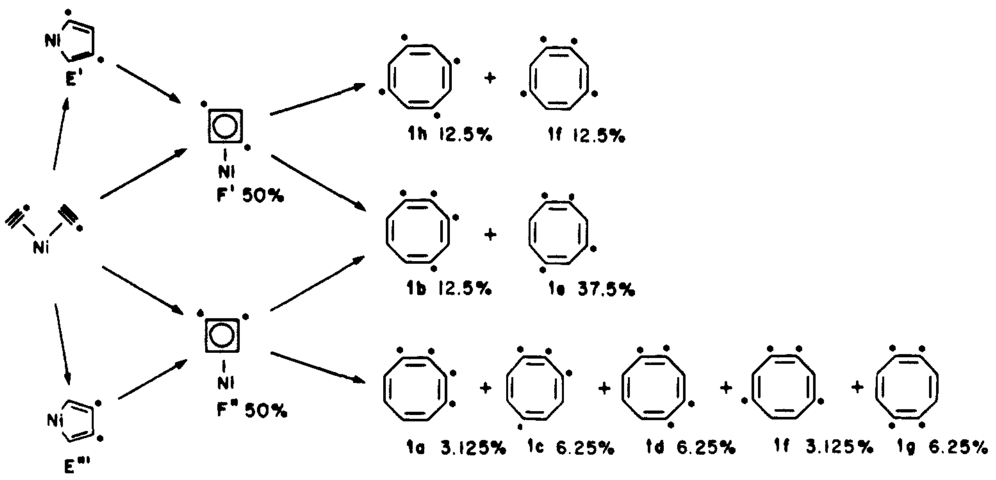
Scheme III



Mechanisms with Cyclobutadiene or Benzene Intermediates. A cyclobutadiene intermediate was proposed as a possibility in a mechanism as early as 1948.[32] A classic paper by Longuet-Higgins and Orgel explicitly suggested the role of metal cyclobutadiene intermediates in the formation of COT.[33a] There are several alternative pathways one might envision including cyclobutadiene as an intermediate.[14,36-38] The critical common species is a nickel cyclobutadiene moiety (see Scheme III). It should be noted that such a complex might derive either directly from a bis(ethyne) species or through the intermediacy of a metallacycle. The latter pathway has precedence both in nickel chemistry[33b] and elsewhere in the transition metals.[33c] The formation of metal cyclobutadiene species from two alkynes has been documented for nickel,[34] although it is more common for other metals.[35] The production of benzene in the reaction also suggests the possible intermediacy of a nickel–arene complex.[15,20,39-42]

Carbyne Intermediates. A fourth type of mechanism involves arbitrary recombination of carbyne units derived from cleavage of the original carbon–carbon triple bond. There has been recent work that suggests alkyne metathesis is common to a variety of transition-metal systems.[43] Carbyne complexes are sometimes isolated although the predominant reaction pathway with excess alkyne is further metathesis.

These four types of mechanisms for the production of COT are not exhaustive in their scope; there is certainly the possibility of more complex mechanisms or the concomitant operation of several pathways. They do, however, provide a framework for analysis of mechanistic possibilities based on known results in organometallic chemistry. Several reviews have been published regarding alkyne oligomerization and transition-metal chemistry.[10,44]

Strategic Considerations. Our work was prompted by consideration of the various ratios of the eight isotopomers of COT that result when produced from a monolabeled ethyne as predicted by topologically distinguishable mechanisms. The expected labeling patterns are summarized in Table I. Double-bond isomers are not differentiated. It should be stressed that the anticipated presence of four labels in the COT is based on the assumption that it is the product of four intact ethyne molecules. Due to the simplicity of ethyne, there are only two monolabel variations one might employ. The first would be the exchange of one hydrogen for another hydrogen isotope. However, this molecule is not a satisfactory probe because the label is likely to be scrambled in the course of the reaction (vide infra). In addition, should carbon–hydrogen bond breaking be rate- and/or product-determining, e.g., as in metal hydride reactions, one would have the additional complication of kinetic isotope effects in the COT formation. A

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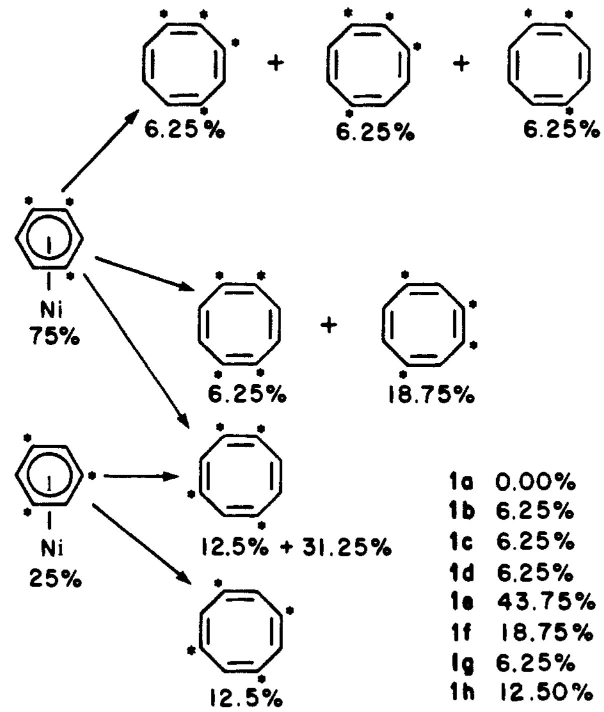
(46) (a) Chini, P.; Palladino, N.; Santambrogio, A. *J. Chem. Soc. C* **1967**, 836. (b) Chini, P.; Santambrogio, A.; Palladino, N. *Ibid.* **1967**, 830. (c) Simons, L. H.; Lagowski, J. J. *J. Org. Chem.* **1978**, *43*, 3247.

Scheme IV



second possibility involves isotopic substitution at one of the carbon atoms such as in ethyne-*1*-^{13}C. This option appears especially attractive because isotopic effects should be negligible.[47] Details of the synthesis of the requisite labeled ethyne have been published.[48] In a process involving alkyne metathesis, there might not only be scrambling of the label, but also the possibility of some COT molecules with both more and less than four labels.

The formation of products from a concerted mechanism may be envisioned in a variety of ways, but perhaps the simplest is to merely consider the four labeled molecules in a circular arrangement as shown in Figure 1. Now each ethyne may be oriented in two distinct ways, thus producing $2^4 = 16$ COT molecules. The distribution leads to no **1a–d**, 50% **1e**, 25% **1f**, and 12.5% each of **1g** and **1h**. While not readily apparent, an identical product distribution will result from any stepwise mechanism. A graphic illustration of the point can be seen in Scheme II where the metallacyclopentadiene and metallacycloheptatriene complexes have been employed as possible intermediates.

As in Whitesides' earlier experiment,[14] the key element of the labeled molecule is to provide a means to distinguish among intermediates which control the extent to which the initial C–C connectivity of the ethyne is maintained in the product. As described above, cyclobutadiene is an example of a potential intermediate ligand. The assumption is made that all four carbon–carbon bonds of the coordinated cyclobutadiene are equivalent.[45a] In such a structure, it becomes impossible to distinguish the pairs of atoms in the C_4 ring that originated from two ethynes. Since all four bonds are equally susceptible to attack, the two atoms derived from any single ethyne need not remain bound to each other in the product molecule.

The most straightforward approach to COT from a metal cyclobutadiene complex derives from a simple dimerization. There are other possible mechanisms involving metal cyclobutadiene complexes. Several of these may be viewed as proceeding through cyclobutadiene intermediates which react further in a stepwise fashion to form products. All such mechanisms containing one cyclobutadiene intermediate will yield an identical distribution of labeled COTs.

If the reaction were to involve a metal benzene complex as an intermediate derived from stepwise cyclotrimerization, there would again be the possibility of an insertion between two carbons derived from a single ethyne unit. This is illustrated in Scheme IV. The reaction products from such a mechanism would lead to the identical distribution as the mechanism that derives from one cyclobutadiene and subsequent stepwise reactions. The numerical results for these mechanisms are listed in Table I under "one symmetric intermediate". In contrast, if the reaction were to involve a metal benzene complex arising from addition of an ethyne to a metal cyclobutadiene, the distribution of products would almost exactly parallel those from cyclobutadiene dimerization, since each of these mechanisms contains two symmetrical intermediates. It should be noted that if the formation of any symmetric intermediate is reversible, then even greater randomization of the label would be introduced.

A topologically significant alternative to any of the previously cited mechanisms is a hypothetical process involving complete scrambling of the carbon label. In such a situation the presence or absence of a label in any given position has equal probability. Hence, all eight isomers would be formed with equal probability. Such a mechanism has been given the designation "random" since products are formed by random cyclization of carbyne units. Such "random" products need not explicitly proceed through carbyne intermediates if, for example, there is a highly fluxional symmetric intermediate which rearranges carbon–carbon bonds.[13a]

Analysis. Our initial intention was to use mass spectrometry to analyze the mixture of COTs produced in the reaction. The parent region would allow for testing whether the COT molecules were in fact derived from four ethyne units. Moreover, since the stepwise or concerted mechanism yields none of the products with three sequential labels, **1a–c**, our intention was to consider C_4 fragments from the COT products; the chance of finding four labels in a row would be zero for the stepwise concerted as well as the one symmetric intermediate mechanism. Also the proportion of fragments with three labels will vary among the different mechanisms.

Results and Discussion

Rieke Nickel Powder Catalyzed Ethyne Cyclizations. The experimental difficulties associated with using ethyne at high pressures prompted us to investigate alternative catalysts for the cyclization reaction which might be effective under ambient conditions. Our initial inquiry centered on the possibility of generation an active nickel(0) species as the catalyst for the reaction. While Chini's work[46] demonstrated the feasibility of using nickel(0) as catalysts for some alkynes, the majority of nickel(0) compounds are not active for ethyne itself.

An active "nickel(0)" slurry of the type developed by Rieke[49] was prepared by the reaction of 2 equiv of potassium with nickel dibromide in THF. When ethyne was bubbled through the resulting black, heterogeneous material, both benzene and COT were formed. Under slow flow conditions at 85–95 °C, benzene predominated over COT by a factor of approximately 4:1, while the catalyst turnover was roughly 3 per day. It was also possible to use nickel chloride or nickel acetylacetonate as precursors.

The nickel-powder-catalyzed cyclization was undertaken in the presence of a stoichiometric amount of triphenylphosphine. As Rieke reported,[49] the activation took place much quicker than without the phosphine present. When this slurry was subjected to ethyne, benzene was produced more rapidly and in larger quantities than without the triphenylphosphine, but COT formation was not completely suppressed. The ratio of benzene to COT was approximately 15:1.

With a catalyst at our disposal which reproducibly synthesized COT and benzene from ethyne, it was of interest to investigate the potential intermediacy of the benzene product in COT formation. For this purpose, benzene-d_6 was added to activated

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catalyst and subsequently exposed to ethyne for 2 days. The COT produced in the reaction was analyzed by mass spectrometry. Unlabeled COT shows an M + 1 peak at *m/e* 105 with about 9% the intensity of the parent peak at *m/e* 104, corresponding to the natural ^{13}C abundance in an eight-carbon molecule. The COT formed in the presence of benzene-d_6 showed *m/e* values at 104, 105, and 106 of relative intensities 100.00:22.90:3.06. There were no peaks between *m/e* 106 and 115 with relative intensity greater than 2%. This result indicated that there was limited carbon–hydrogen (deuterium) scrambling taking place but that the C_6D_6 unit does not become incorporated intact into product COT under the reaction conditions. Meriwether had previously observed hydrogen–deuterium exchange in the reaction of 1-heptyne-*1-d* and 1-pentyne with bis(triphenylphosphine)dicarbonylnickel in boiling cyclohexane.[28]

The results of the cyclization reactions with Rieke nickel powder were important because they suggested that "nickel(0)" species were capable of catalyzing the cyclotetramerization reaction. Observation of hydrogen–deuterium exchange provided further validation for our selection of ethyne-*1*-^{13}C for our labeled experiment. Nevertheless, the nickel powder did not satisfy our synthetic goals; both the turnover rates and yields were too low for our purposes. Thus, we turned to a modification of the Reppe catalytic system for further experiments.

Small-Scale Cyclizations. Since we would be working with small amounts of ethyne, we focused attention on the problem of preparing manageable quantities of COT from small-scale reactions of ethyne. As a catalyst system, we used a mixture of nickel acetylacetonate and calcium carbide in THF, almost identical with that of Cope[4] and Schrauzer[5] in their early studies. Reactions were carried out in Fischer–Porter bottles under a nitrogen atmosphere pressurized to between 50 and 100 psi at 85–90 °C. Best results were obtained with 2–3% nickel acetylacetonate and 11–13% calcium carbide. Use of higher proportions of catalyst led to a greater benzene production relative to COT. The reactions were usually allowed to proceed for 2 days. During the first day, there was an apparent activation process which resulted in the formation of finely divided, black particulate matter in the THF. Typically no COT was observed until after this phenomenon transpired. It was possible to convert 89% of the ethyne in a 6-mmol scale reaction to 0.85 mmol of COT (56%) and 0.7 mmol of benzene (33%). Attempts to scale down the reaction were less successful.

Several variations of the basic catalytic system were attempted. One concern which we had was that some of the calcium carbide might react with trace amounts of water to yield ethyne, thus diluting the isotopic enrichment of the label. Although this fear was unfounded (vide infra), we wished to use a system that did not require the calcium carbide. Use of nickel cyanide or ethylene oxide as a cocatalyst[1] with nickel acetylacetonate,[25,52] although successful, did not lead to high conversions and yields.

In the search for a more efficient system, we turned our attention to other reducing agents. Aluminum and boron species have been employed as cocatalysts (or activators) for the cyclotetramerization reaction.[52] We have found diethylaluminum ethoxide to be a successful coingredient with nickel acetylacetonate. This catalyst had several positive characteristics. It was more selective for COT than any of the other systems studies in our laboratories. Moreover, the system was active even when the scale of the reaction was as small as 3 mmol. Another feature of note was the color changes which took place upon addition of the aluminum reagent to a stirred solution of the nickel acetylacetonate in THF. The initial color of green turned yellow then orange and proceeded to successively deeper colors of brown and finally black. Typically, the aluminum reagent was added dropwise until the solution turned orange (approximately 1 equiv per nickel). All these changes transpired in the absence of ethyne in marked contrast to the induction period observed for all other systems with the exception of the potassium reduction of nickel acetylacetonate. These results are consistent with the requirement of a reduced nickel species as a key intermediate in the catalytic cycle.

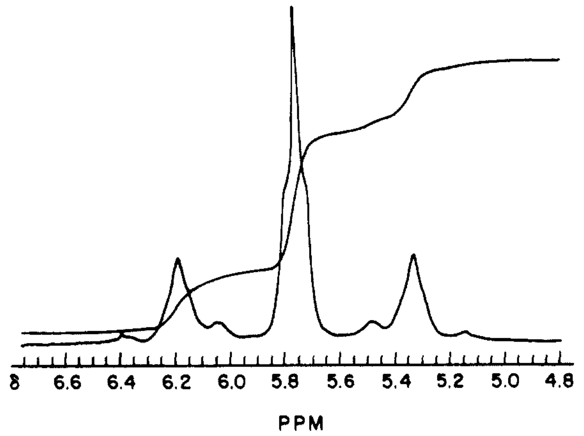

Figure 2. ^1H NMR spectrum of COT derived from $HC{\equiv}{}^*CH$.

Table II. Calculated and Observed Abundance of $C_4H_n^+$ Ions

mass	stepwise or concerted	one symmetric intermediate	cyclobutadiene dimerization	random	exptl
50	0.001	0.002	0.007	0.023	0.031
51	0.191	0.232	0.260	0.305	0.418
52	1.327	1.295	1.274	1.243	1.441
53	1.861	1.793	1.748	1.678	2.358
54	1.000	1.000	1.000	1.000	1.000
55	0.192	0.214	0.233	0.267	0.244
56	0.019	0.021	0.025	0.037	0.028

Analysis of Labeled COT. The COTs derived from both the nickel acetylacetonate/calcium carbide and nickel acetylacetonate/diethylaluminum ethoxide catalyst systems with ethyne-*1*-^{13}C exhibited mass spectral data consistent with the incorporation of four intact ethyne units in the tetrameric product. This result rules out any kind of carbon scrambling process which might take place during the cyclization.

As expected, the ^1H NMR spectrum of the labeled COT did not lend itself to simple analysis. The key portion of the ^1H NMR spectrum (600 MHz) is reproduced in Figure 2. The value of J_{C-H} of 155.6 Hz agreed well with the literature value of 155 Hz.[50] The ^{13}C NMR spectrum was a single, broad signal.

For the reasons outlined previously, our first attempt to analyze the COT mixture was by means of the $C_4H_n^+$ fragment ions. There is a reasonable intensity for such ions in COT itself. After subtraction of the natural ^{13}C isotope influence, one may generate an "envelope" of peak intensities for the $^{12}C_4H_n^+$ ions in the COT spectrum. The values incorporated in the calculations were normalized to the $C_4H_4^+$ ions: $C_4H_2^+$, 1.5; $C_4H_3^+$, 2.2; $C_2H_4^+$, 1.0; $C_4H_5^+$, 0.08; $C_4H_6^+$, 0.01. After incorporation for isotopic abundance, Table II results; the numbers in Table II have been normalized to the peak at *m/e* 54 which corresponds primarily to $^{12}C_2{}^{13}C_2H_4^+$.

The experimental numbers recorded in Table II derive from an experiment with 99.2% ^{13}C isotopic enrichment and catalytic in nickel acetylacetonate–diethylaluminum ethoxide. While these numbers did not agree particularly well with any of the mechanisms proposed, they were suggestive of a pathway with significant randomization. Because of the envelope calculation, the ratios for *m/e* 54–56 should be the most important in that they are least affected by the fragmentation patterns. Labeled COT derived from a different experiment employing the catalyst system of nickel acetylacetonate and calcium carbide produced similar results.

The results in Table II differ significantly from those obtained independently by chemical degradation. We suspected this was due to skeletal rearrangement processes in COT on electron im-

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[52] Pirzer, H.; Beck, F. Ger. Pat. 1 092 908, 1960. Chukhadzhyan, G. A.; Abramyan, Z. I.; Grigoryan, V. G.; Avetisyan, D. V. *Arm. Khim. Zh.* **1970**, 860. Luttinger, L. B. *Chem. Ind. (London)* **1960**, 1135. Luttinger, L. B. *J. Org. Chem.* **1962**, *27*, 1591. Green, M. L. H.; Nehmé, M.; Wilkinson, G. *Chem. Ind.* **1960**, 1136. Giacomelli, G.; Caporusso, A. M.; Lardicci, L. *J. Org. Chem.* **1979**, *44*, 231.

Scheme V

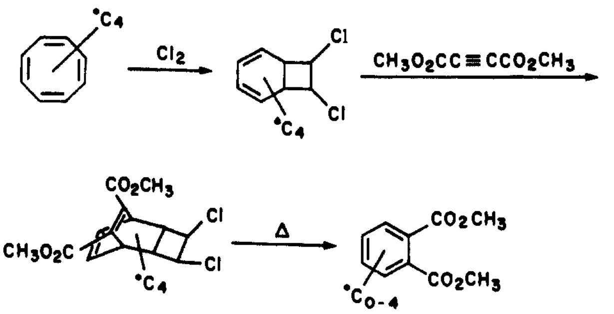

Table III. Calculated and Experimental Relative Peak Intensities for the $M^+ - OCH_3$ Ion Peak of Dimethyl Phthalate Containing Varying Amounts of Label according to Several Mechanisms

mass	stepwise or concerted	one symmetric intermediate	cyclobutadiene dimerization	random	expt1[a]
163	0.6	0.8	1.5	3.6	2.9 ± 0.1
164	22.4	28.2	31.7	36.5	21.1 ± 0.6
165	100.0	100.0	100.0	100.0	100.0
166	23.6	29.2	32.6	37.3	22.8 ± 0.4
167	1.9	2.3	3.1	5.2	1.3 ± 0.5

[a] Average of five runs including standard deviation. The mass spectral line intensities ranged from 900 to 2200 counts for the smallest *m/e* 167, 97% ^{13}C isotopic enrichment.

pact, leading to label scrambling prior to fragmentation. The skeletal rearrangement of ions and their subsequent fragmentation has been well documented for species such as C_7H_8 isomers.[53] For example, toluene, 1,3,5-cycloheptatriene, and spiro[2,4]hepta-1,3-diene dissociate under electron impact to the tropylium ion. Previous workers have examined the effect of molecular structure on ionic decomposition for seven C_8H_8 compounds including COT.[54] While they do not explicitly mention skeletal rearrangement, they argue that, in most instances, molecular and fragment ions from these isomers appear to have the same structure. It is beyond the scope of this work to explicitly detail the manner of rearrangement of the molecular ion prior to fragmentation, but investigators in other laboratories indicate some possible pathways.[55,56]

The classic method which allows one to determine the connectivity in molecular frameworks is chemical degradation. Thus, our aim was to use a high-yield means of converting the labeled COTs into one or perhaps two four-carbon fragments which might be analyzed by mass spectrometry. Fortunately, such methodology was already present in the literature, exemplified by the synthesis of *cis*-3,4-dichlorocyclobutene and dimethyl phthalate from COT.[57] The series of reactions is illustrated in Scheme V.

The reaction sequence was particularly advantageous since no special purification of the COT mixture was necessary. The THF solvent, originally employed in the cyclization, was exchanged for pentane. Carbon tetrachloride was added from which pentane could be evaporated. The chlorination was carried out on a metal vacuum line to facilitate the monitoring of chlorine uptake with a Bourdon gauge. The reaction was also checked by gas chromatography both via the disappearance of COT as well as the appearance of both the *cis*- and *trans*-dichlorobicyclooctadienes. The product mixture was then allowed to react with an excess of dimethyl acetylenedicarboxylate. The pyrolysis of the resulting adduct could then be carried out directly at 250–300 °C in the injector port of a gas chromatograph connected to a mass spectrometer.

Table IV. Calculated and Experimental Peak Intensities for the $M^+ - OCH_3$ Ion Peak of Dimethyl Phthalate

mass	stepwise or concerted	one symmetric intermediate	cyclobutadiene dimerization	random	exptl[a]
163	3.0	3.6	4.6	7.2	7.0
164	38.1	43.5	46.8	51.2	36.5
165	100.0	100.0	100.0	100.0	100.0
166	21.8	26.5	29.5	33.7	20.4
167	1.8	2.1	2.7	4.4	1.2

[a] 90% ^{13}C isotopic enrichment.

Since these reactions were undertaken on a small scale, it was easier to analyze for the dimethyl phthalate product, readily separated from the rest of the reaction components, than for the dichlorocyclobutene. The resulting theoretically expected label distributions for the various mechanisms are contrasted in Table III with the experimentally observed numbers for a reaction undertaken with 95% ^{13}C isotopically enriched ethyne-*1*-^{13}C. The numbers have been normalized to the most abundant fragment, *m/e* 165, which corresponds to an ion with two ^{13}C atoms.

Another set of data was obtained when the reaction was undertaken with a different catalyst and with only 90% ^{13}C-isotopic enrichment of the ethyne. These results are compiled in Table IV. Tables III and IV share a startling resemblance in that the agreement with the stepwise or concerted mechanism is excellent. The only significant deviation is observed for *m/e* 163 which experimentally has too large a value. It should be noted that *m/e* 163 corresponds to the peak associated with completely unlabeled dimethyl phthalate. Such an "impurity" might conceivably derive from an injector port reaction of the ubiquitous stabilizer octyl phthalate. If the extra intensity at *m/e* 163 does correspond to such an "impurity", in each case it only requires approximately 2% of the material to account for the entire discrepancy. In both experiments, the experimental value of *m/e* 167 is significantly low in relative terms. However, on an absolute basis, the differences is less than 1% of the most abundant fragment (*m/e* 165). Moreover, the largest errors would be expected for the mass 167 due to its weaker intensity.

The numbers depicted in Tables III and IV provide strong support for a concerted or stepwise mechanism in the Reppe COT synthesis. More significantly, they rule out a large number of alternative reaction pathways. The numbers are incompatible with the presence of a symmetric intermediate either in the form of cyclobutadiene or benzene. Furthermore, our results are even more at odds with a mechanism which produces randomly labeled COT.

Error Analysis and Conclusion. The conclusions from any work which depends so highly on the quantitative comparison of ratios from experimentally derived numbers must consider the possible influence of errors both systematic and random in nature.

It was independently determined that no dilution of the isotopic enrichment occurs in the preparation of labeled ethyne. Mass spectrometer effects due to ionizing statistics,[58] threshold levels,[59] or small variations in temperature or magnetic drift were minimal. Possible kinetic and/or thermodynamic ^{13}C isotope effects should be small.[47]

None of the possible errors cited could lead to the changes in magnitude that are required to cast severe doubt on the agreement between the observed ratios and those calculated for a stepwise or concerted mechanism. There is no evidence suggestive of some mixture of topologically differentiated pathways. Since the same

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(60) American Petroleum Inst. *Selected Mass Spectral Data*; Hydrocarbon Publications: College Station, TX 1979.

mechanistic implications were obtained when using a nickel(II) catalyst precursor in the presence of calcium carbide as with the identical nickel complex in the presence of an aluminum reagent, one might conclude that the active catalytic species are similar. Ostensibly, nickel(0) species derived from potassium and nickel(II) compounds are capable of catalytic activity in the Reppe cyclotetramerization reaction. Our work does not address the question of whether the catalyst is mononuclear, dinuclear, small cluster, or surfacelike in nature, although it places severe restrictions on the symmetries available to the organometallic intermediate species in the cyclization reaction. The results effectively rule out the significant occurrence of cyclobutadiene, random, and metal-benzene pathways to COT from ethyne and nickel catalysts.

Experimental Section

General Procedure. All reactions were routinely carried out under an atmosphere of dry nitrogen with glassware oven-dried at 150 °C. All boiling points are uncorrected. Proton NMR spectra were recorded on a Varian T-60, a Varian EM-390, or a UCB-250 spectrometer. The UCB-250 uses a Nicolet 1180 data system and has a Cryo Magnet Systems 5.7-T magnet. The ^{1}H NMR spectrum of COT $^{13}C_4$ was also recorded on a 600-MHz spectrometer at the regional facility of the University of Pittsburgh. Chemical shifts are reported in parts per million downfield of internal tetramethylsilane (Me_4Si) or referenced to the C_6D_5H peak 7.15 ppm downfield from Me_4Si. Mass spectral data were collected on an AEI-MS-12 (low resolution) or Du Pont CEC 21-110B (high resolution) instrument by the Mass Spectral Service at the University of California, Berkeley. Elemental analyses were carried out by the Microanalytical Laboratory. Analytic gas chromatography was performed on Hewlett-Packard 5710A and Hewlett-Packard 5880A flame ionization detector instruments. The former employed a 10 ft × $^1/_4$ in. 20% UCW 98 on 60/80 mesh Chromosorb W column. The latter was equipped with a 2 ft × 6 mm 2% OV-101 on 100/120 mesh Chromosorb W column and a 12 m × 0.2 mm methylsilicone-coated fused silica capillary column. Preparative gas chromatography was carried out on a Varian 920 with a 8 ft × $^1/_4$ in. 20% SE-30 on Chromosorb W column. Coupled gas chromatography/mass spectral (GCMS) data were undertaken with a Finnigan 4000 machine in conjunction with an Incos data system. A variety of both glass and silica capillary columns were used with common-packing materials such as SP2250 and SE-54. All spectra were obtained at 70 eV unless otherwise indicated. A Vacuum Atmospheres drybox equipped with a HE-493 Dri-Train catalyst and a freezer was used for storage and transfer of air-sensitive materials.

THF and diethyl ether were routinely distilled from sodium benzophenone ketyl. Dichloromethane was distilled from P_2O_5. Other solvents were purified by standard procedures, though special care was taken to remove peroxides from ethers. High-purity chlorine gas from Matheson Co. was used directly without further purification.

Cyclization of Ethyne with Nickel Dibromide and Potassium in THF. Method A. Nickel dibromide (3.06 g, 0.017 mol) was partially dissolved in freshly distilled THF (25 mL). The solution was purple in color but the undissolved solid nickel dibromide retained its orange color. Potassium metal (1.33 g, 0.034 mol) was added to the stirred solution at room temperature. The solution was then heated to reflux overnight to obtain the black "Ni(0)" slurry.[49] In all successful cyclizations of ethyne to cyclooctatetraene, a similar black, heterogeneous material was present. Thus, the appearance of such material was often associated with an activation of the catalyst. Ethyne was admitted to the stirred solution, at room temperature, after passage through two −78 °C traps by means of a syringe needle penetrating a septum into the liquid. The reaction was monitored by the periodic removal of aliquots. These aliquots were filtered in air and subsequently the filtrates were injected onto a FID gas chromatograph. After 2 h there were only small indications of product. By 5 h, both benzene and COT were clearly visible in the chromatogram; the benzene predominated by a least 4:1 over the COT. Both the benzene and cyclooctatetraene peaks were confirmed by co-injection with authentic samples. There was also an indication of another tetramer peak in the chromatogram on the basis of its retention time. This compound, possibly styrene, integrated to less than 10% of the COT. No additional efforts were made to identify this material. Such formation of benzene and COT was reproducible. In a subsequent experiment, it was noticed that if ethyne was bubbled through the solution of nickel salt and THF immediately after the potassium addition that black particular matter appeared as soon as 1.5 h later, possibly indicative of enhanced solvation.[61] The effect of increased temperature was to increase the rate of oligomerization. Decane was used as an internal GLC standard to monitor the production of oligomers. After GLC calibration of the benzene, cyclooctatetraene, decane system, it was determined that the nickel slurry was catalytic although the turnover rate was very low (approximately 3 mol of COT/mol of Ni/day).

Cyclization of Ethyne with Nickel Dibromide and Potassium in THF. Method B. A 115-mL Fischer–Porter bottle was loaded with anhydrous nickel dibromide (0.50 g, 2.29 mmol) in a Vacuum Atmospheres glovebox. A solution of freshly distilled THF (35 mL) was added by syringe. The closed system was heated for 2.5 h at 100 °C to maximize the solubility of the nickel salt in the solution. Potassium metal (0.183 g, 4.58 mmol) was then added in the drybox. The bottle was pressurized with ethyne to 15–20 psi. Two stainless steel traps at −78 °C were used to trap the acetone from the ethyne. The presence of such traps was shown to be necessary to obtain COT production, although the Rieke nickel slurry was able to produce benzene in the presence of acetone. With the traps present, the black color characteristic of active catalyst appeared after 1.5 h at 90 °C. The reaction was not monitored but was run for 2 days with periodic repressurization of the ethyne. As in Method A, the reaction was filtered and the filtrate subsequently was analyzed for products by GLC. In a typical experiment, the ratio of benzene to COT was 7.5:1.

Cyclization of Ethyne with Nickel Dibromide and Potassium in Diglyme. The nickel(0) slurry was prepared as in Method A. The THF was then evaporated by vacuum transfer. Peroxides in the diglyme were removed either by refluxing in cuprous chloride or by passing the diglyme through a short column of alumina. The diglyme was then distilled from sodium. Diglyme (approximately 25 mL) was added to the black, amorphous material and ethyne was added as in Method A, while the temperature of the reaction was maintained between 110 and 120 °C. Under these conditions, COT was present in significant quantities in the reaction mixture, but there was no detectable benzene.

Cyclization of Ethyne with Nickel Dibromide and Potassium in the Presence of Phosphine. The reaction was undertaken in the presence of a stoichiometric amount of triphenylphosphine (mmol of $NiBr_2$ = mmol of PO_3). Immediately upon addition of triphenylphosphine to the solution of $NiBr_2$ and THF, the solution turned from purple to green. The activation of the system with the potassium took place more rapidly (which is also found in Rieke's systems[49]) and the slurry produced was subjected to ethyne in the same manner as in Method A. In this experiment, benzene is produced at 2–3 times the rate of the reaction without the added phosphine as determined by GLC integration of peaks from aliquots removed from both reactions at the same time intervals. COT formation is suppressed; the ratio of benzene to COT was approximately 15:1.

Cyclization of Ethyne with Nickel Dibromide and Potassium in the Presence of Benzene-d_6. The nickel dibromide/potassium catalyst system was prepared as in Method B. The nickel dibromide (0.774 g, 3.53 mmol) was reacted with an 8% excess of potassium (0.300 g, 7.67 mmol). After the catalyst was activated, benzene-d_6 (0.8 mL, 8.3 mmol) was added. In the COT produced in this experiment, the intensity ratios of the signals in the mass spectrum for masses 104, 105, and 106 were 100.00:22.90:3.06 as compared to normal COT where the ratios are 100.00:8.97:0.01. There were no peaks between *m/e* 106 and 115 with relative abundance greater than 2%. The presence of mass spectrum peaks corresponding to *m/e* 127–130 [127 (3.21), 128 (9.37), 129 (12.92), 130 (11.08)] was suggestive of the formation of pentamer.

General Small-Scale Ethyne Cyclization Reaction. The nickel catalyst was added to a 115-mL Fischer–Porter bottle in the drybox. The bottle was attached to the vacuum line and freshly distilled dry THF was vacuum-transferred into the reactor. The ethyne (50–150 mL, 2–6 mmol) was than vacuum transferred from a bath at −78 °C into the reactor. While still cold, the bottle was attached to a stainless steel line connected to a nitrogen cylinder. The reaction was pressurized with nitrogen to between 50 and 60 psi. The system was then isolated (i.e., disconnected from the nitrogen line), allowed to warm, and heated at 85–90 °C for 2–3 days. Activation of the catalyst to a black, heterogeneous solution usually occurred during the first 18 h (but see below for specific examples). The workup of the reaction simply involved the release of the nitrogen pressure and filtration in air. Preliminary results were obtained using gas chromatography as well as gas chromatography/mass spectrometry. In some cases, further purification was effected by a pentane/water wash, evaporation of the majority of the pentane, and preparative gas chromatography.

Cyclization of Ethyne with Nickel Acetylacetonate and Calcium Carbide. The reaction was sensitive to scale. Best results were obtained with

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(61) Numerous researchers have found that the presence of the alkyne during the reduction has an impact on the activity of the catalyst. See, for example, ref 52.

(62) Schunn, R. A. *Inorg. Synth.* **1974**, *15*, 5.

Ni(acac)$_2$ (0.043 g, 0.17 mmol), CaC$_2$ (0.05 g, 0.78 mmol), and ethyne (135 mL, 6 mmol). In this case a conversion of almost 89% of the ethyne was obtained, resulting in 56% COT (0.85 mmol) and 33% benzene (0.7 mmol), determined by comparison with decane in a calibrated GC integration. Attempts to scale down the reaction to 2 mmol of ethyne with 15 mg of Ni(acac)$_2$ and 16 mg of CaC$_2$ were generally not successful. Higher percentages of catalyst tended to promote benzene formation relative to cyclooctatetraene formation.

In the specific ethyne-*1*-^{13}C experiment for which mass spectral intensities are reported below, the ratios of materials were as follows: lithium hexamethyldisilazide (5.312 g, 22.5 mmol), nickel acetylacetonate (0.036 g, 0.14 mmol), calcium carbide (0.038 g, 0.59 mmol), triglyme (30 mL), triethylene glycol (6 mL, 45 mmol), and a solution of 1,2-dibromoethane-*1*-^{13}C containing approximately 7% pentane by weight (1.091 g, 5.8 mmol). The reaction was maintained at 87 °C, 85 psi, for 50 h.

Product mixtures were analyzed by GLC/mass spectrometry. Comparison of the mass spectral data obtained for the reaction of both labeled and unlabeled ethyne is presented below.

Chromatogram from unlabeled ethyne cyclization with mass spectra presented as *m/e* (relative intensity). Column conditions were 45 °C for 2 min followed by heating at 3 °C/min. Peak 1 (retention time 7 min 56 s): 78 (M$^+$, 100), 77 (25.8), 76 (5.8), 52 (48.4), 51 (33.7), 50 (29.7). Peak 2 (retention time 8 min 12 s): 78 (M$^+$, 100), 77 (23.0), 52 (22.9), 51 (24.2), 50 (21.8). Peak 3 (retention time 10 min 31 s): 92 (M$^+$, 47.8), 97 (28.6), 67 (26.9), 63 (10.1), 39 (17.9). Peak 4 (retention time 10 min 42 s): 98 (M$^+$, 47.8), 97 (28.6), 67 (26.9), 57 (41.9), 56 (100.0), 55 (52.5), 42 (86.9), 41 (87.9). Peak 5 (retention time 12 min 6 s): 100 (M$^+$, 17.1), 85 (27.0), 43 (100.0). Peak 6 (retention time 17 min 1 s): 104 (M$^+$, 97.1), 103 (65.6), 78 (100.0), 77 (45.0), 52 (22.3), 51 (50.4), 50 (33.3), 39 (31.6).

Chromatogram from labeled ethyne cyclization. Peak 1′ (retention time 1 min 7 s): 81 (M$^+$, 100.0), 80 (47.7), 79 (12.9), 54 (45.6), 53 (40.8), 52 (50.5). Peak 2′ (retention time 10 min 27 s): 81 (M$^+$, 100.0), 80 (43.4), 78 (51.7), 77 (16.8), 54 (19.5), 53 (28.0), 52 (35.7), 50 (20.7). Peak 3′ (retention time 13 min 26 s): 92 (M$^+$, 59.7), 91 (100.0), 65 (14.2), 39 (12.0). Peak 4′ (retention time 13 min 41 s): 99 (M$^+$, 45.5), 98 (28.3), 68 (24.6), 58 (37.9), 57 (93.6), 56 (60.4), 43 (48.4), 42 (100.0). Peak 5′ (retention time 14 min 57 s): 100 (M$^+$, 16.7), 85 (27.6), 43 (100.0). Peak 6′ (retention time 21 min 7 s): 108 (M$^+$, 100.0), 107 (94.1), 106 (32.4), 81 (85.7), 80 (70.2), 54 (24.4), 53 (55.0), 52 (41.8), 40 (37.7). Peaks 1 and 2 are trimers of the ethyne. Peak 1 which is a very minor peak is likely the *cis*-1,3-hexadien-5-yne, while peak 2 is benzene. Peak 3 corresponds to toluene. Peak 4 probably derives from the addition of one ethyne unit to THF. Peak 5 corresponds to 2,4-pentanedione, and peak 6 is COT.

Cyclization of Ethyne with Recycled Catalyst. All the volatile material was removed from the reaction initiated with nickel acetylacetonate and calcium carbide. Fresh THF (25 mL) and ethyne (136 mL, 6 mmol) were added and the reaction was allowed to proceed as described for the general small-scale cyclization reaction. This catalyst was still active in the production of COT (11% conversion, 0.168 mmol) as well as benzene (<10% conversion), but it was less efficient than the initial catalyst.

Cyclization of Ethyne with Nickel Acetylacetonate and Diethylaluminum Ethoxide. Nickel acetylacetonate (0.030 g, 0.12 mmol) was loaded into the Fischer–Porter bottle in the usual fashion. The diethylaluminum ethoxide reagent may be either added to the THF solution of Ni(acac)$_2$ or the THF may be vacuum-transferred into the reactor followed by syringe addition of the aluminum reagent to the stirred mixture. The second method was preferable because it allowed a more direct monitoring of the color changes apparently associated with catalyst reduction–activation; the initial green solution turned yellow, then orange, and last brown and black. Usually it sufficed to add between 10 and 20 mg (0.03–0.16 mmol) of the aluminum reagent to reach the orange color which was the optimum point of addition. On standing, the solution would continue to change in color after the addition was completed. After the addition of ethyne by the usual procedure, the reaction was allowed to proceed for 1 day at 85 °C. The nickel acetylacetonate/diethylaluminum ethoxide catalyst was more selective for COT formation than the corresponding nickel acetylacetonate/calcium carbide catalyst (COT to benzene >10:1) but the overall conversion of ethyne was not as efficient.

The mass spectra of the COT derived from ethyne and ethyne-*1*-^{13}C are as follows *m/e* (intensity): ethyne, 104 (M$^+$, 87.4), 103 (60.1), 78 (100.0), 77 (43.4), 52 (20.4), 51 (79.8), 50 (4o.4), 39 (74.0); ethyne-*1*-^{13}C, 108 (M$^+$, 100.0), 107 (73.2), 81 (88.4), 80 (61.3), 54 (31.9), 53 (75.2), 52 (45.9), 41 (29.7), 40 (50.31).

Chemical Degradation of Cyclooctatetrane. The degradation of the cyclooctatetraene formed from ethyne was performed according to a modification of the procedure developed for the synthesis of *cis*-3,4-dichlorobutene.[57] The mixture of the products from the Reppe cyclization reaction was washed with a single large amount of water (approximately 500 mL) to take up the THF. Pentane (3-mL aliquots) was used to extract all organic material from the water. When extraction was complete, the pentane was exchanged for carbon tetrachloride by addition of CCl$_4$ followed by evaporation of the majority of pentane. The addition of measured amounts of decane allowed the determination of the exact amount of cyclooctatetraene present by GLC. The solution of COT in carbon tetrachloride was thoroughly degassed on the vacuum line. The flask was then transferred to a metal vacuum line where the uptake of chlorine could be monitored by a Bourdon pressure gauge. The volume of the line was determined prior to the reaction by releasing known volumes of air into the evacuated system. The chlorine was added at −30 °C and the extent of the reaction could be checked by gas chromatography both in disappearance of the COT and formation of the products. The reaction mixture was then heated to reflux for several hours in the presence of an excess of dimethyl acetylenedicarboxylate. The crude Diels–Alder adduct could be subjected to pyrolysis in the injector part of the gas chromatography at 250–300 °C. The mass spectrum of the resulting dimethyl phthalate was then used for analysis.

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Registry No. Ni, 7440-02-0; Ni(acac)$_2$, 3264-82-2; CaC$_2$, 75-20-7; ethyne, 74-86-2; cyclooctatetraene, 629-20-9; diethylaluminum ethoxide, 1586-92-1.

Supplementary Material Available: Further details of statistical and error analysis are included; additional experimental data on Rieke nickel powder reactions are also available (10 pages). Ordering information is given in any current masthead page.