(ring) distances vary over a very small range (1.417 (4)–1.430 (4), 1.490 (5)–1.512 (5), and 2.375 (3)–2.400 (3) Å, respectively). So the pentamethylcyclopentadienyl rings coordinate in a true η^5 way to the metal.

An interesting feature is the deviation (Δ) of the methyl groups out of the plane of the ring and away from titanium, which varies from 0.01 (2) to a maximum of 0.40 (1) Å.[41] Especially the large values of Δ for the methyl groups that contain atoms C_{12} and C_{20} of 0.31 (1) and 0.40 (1) Å, respectively, are noticed here. It is evident that they are caused by the methyl–methyl contacts between the staggered Cp* ligands. These large deviations correspond with the shortest nonbonded intramolecular C–C distances of 3.196 (6) Å. It is interesting to note that in $Cp^*_2Ti(\eta^2\text{-}C_2H_4)$ α and Δ_{max} are almost the same.[40d]

The important contribution of steric crowding is also reflected in the rather long Ti–Cl distance of 2.363 (1) Å that does not differ much from those found in $Cp^*_2TiCl_2$ (Ti–Cl = 2.352 (1) and 2.346 (1) Å respectively) and is also comparable with that in $(CH_2)_3(C_5H_4)_2TiCl_2$ (Ti–Cl = 2.368 (4) Å),[42] CpCp*$TiCl_2$ (Ti–Cl = 2.3518 (9) Å),[43] or Cp_2TiCl_2 (Ti–Cl = 2.364 (2) Å).[44] On the other hand a significant difference is observed, when the Ti–Cl distance is compared with the range of 2.526–2.566 Å observed in the dimeric analogues of **1**, $(Cp_2Ti(\mu\text{-}Cl))_2$ and $(Cp'_2Ti(\mu\text{-}Cl))_2$.[17] In **1** the shortest Ti–Ti distance between the monomeric units is 7.496 (8) Å; this also makes it clear why antiferromagnetic coupling is not observed in **1** (vide supra): the d^1 centers are too far apart. Finally all hydrogen atoms could be located. Their positions and bond angles are comparable with those of normal sp^3-hybridized carbon atoms. The shortest nonbonded intermolecular distance is between Cl and H(63) (2.82 (4) Å) and is similar to that found in $Cp^*_2TiCl_2$.

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Registry No. **1**, 73348-99-9; **2**, 107495-35-2; **3**, 107495-36-3; **4**, 96289-67-7; **5**, 107495-37-4; **6**, 107495-38-5; **7**, 107495-39-6; $TiCl_3(THF)_3$, 18039-90-2; Cp*MgCl(THF), 107495-40-9.

Supplementary Material Available: Tables of hydrogen atom coordinates, anisotropic thermal parameters, least-squares planes and deviations therefrom, and additional bond distances and angles and PLUTO and ORTEP drawings of Cp^*_2TiCl (**1**) (7 pages); a listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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Structures and Rearrangement Mechanisms for Some Bicyclo[6.1.0]nona-2,4,6-triene Complexes of Chromium, Molybdenum, and Tungsten

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The structures of (bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum and (*endo*-9-bromobicyclo[3.1.0]nona-2,4,6-triene)tricarbonylmolybdenum have been investigated by X-ray crystallography. The first crystallized in the orthorhombic space group *Pnma*: $a = 14.185$, $b = 10.417$, $c = 7.230$ Å; $Z = 4$; 1143 reflections were measured, of which 756 were considered observed; the final structure had $R = 0.115$ and $R_w = 0.137$. The second complex crystallized in monoclinic space group $P2_1/m$: $a = 8.740$, $b = 10.038$, $c = 13.742$ Å; $\beta = 85.9°$; $Z = 4$; 1736 reflections were measured, of which 1494 were considered observed; $R = 0.068$ and $R_w = 0.077$. Both are shown to have geometries in which the cyclopropane ring is syn to the metal. In the 9-bromo complex only two of the three C=C bond are coordinated to the metal; the third coordination site is occupied by the halogen. The mechanism of thermal rearrangement of (bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum to (bicyclo[4.2.1]nona-2,4,7-triene)tricarbonylmolybdenum has been investigated by deuterium-labeling and kinetic studies. A new, degenerate rearrangement of the starting complex has been discovered in the course of this investigation. Similar processes are shown to occur for the corresponding chromium and tungsten complexes. It is concluded that both types of rearrangement are sigmatropic processes in which the metal does not directly participate in cleavage of the C–C bond. The difference in thermal chemistry of the complexed and uncomplexed hydrocarbon is proposed to be due to selective inhibition of certain reaction pathways by the metal.

Introduction

The thermal rearrangement of (bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum to (bicyclo[4.2.1]nona-2,4,7-triene)tricarbonylmolybdenum, characterized by Grimme[1] as shown in Scheme I, is an intriguing reaction. It is a rearrangement that does not occur for the uncomplexed hydrocarbon,[2,3] which, instead, undergoes only epimerization and rearrangement to *cis*- and *trans*-8,9-dihydroindenes. The chromium[4] and tungsten[5] com-

(1) Grimme, W. *Chem. Ber.* **1967**, *100*, 113.
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(3) Baldwin, J. E.; Andrist, A. H.; Pinschmidt, R. K. *J. Am. Chem. Soc.* **1972**, *94*, 5845.

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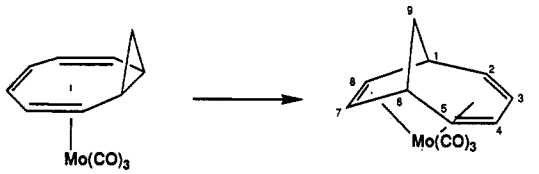
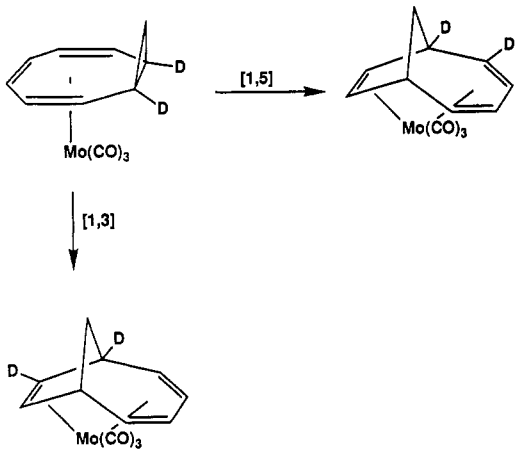
Scheme I. Original Characterization of the Conversion of (Bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum to (Bicyclo[4.2.1]nona-2,4,7-triene)tricarbonylmolybdenum



Scheme II. Discrimination between Formal [1,3] and [1,5] Shifts by Use of a Deuterium-Labeled Reactant



plexes apparently behave like the molybdenum complex. Related reactions for the molybdenum tricarbonyl complexes of bicyclo[6.2.0]deca-2,4,6-triene[5] and a number of propellanes[6] are also known. In each case, the apparent sigmatropic migration of a carbon across the face of a ring anti to the site of coordination of the $M(CO)_3$ moiety would be an event for which there is little other precedent in organometallic chemistry and of considerable significance for that reason. It was this fact that prompted the present mechanistic investigation.

Mechanism of Rearrangement

Results. A reasonable first step in the mechanistic dissection of the reaction seemed to be to determine whether the rearrangement followed a formal [1,3] or [1,5] sigmatropic pathway. These can be distinguished by a labeling experiment, using bicyclo[6.1.0]nona-2,4,6-triene-*1,8-d_2* (**1-d_2**). The outcome of the two rearrangements is shown in Scheme II.

Synthesis of **1-d_2** was achieved by the route summarized in Scheme III.

Rearrangement of the molybdenum tricarbonyl complex of **1-d_2** was investigated at temperatures between 125.0 and 185.7 °C. In each case the label was found predominantly at the sites expected for the formal [1,5] shift. If the total label is defined as 200%, then, at 160.5 °C, 93.2% was found at C1/C6, 93.3% at C2/C5, 6.7% at C3/C4, and 6.9% at C7/C8.[7] The amount of deuterium at the minor sites varied from 4.6% at 125.0 °C to 8.3% at 185.7 °C but

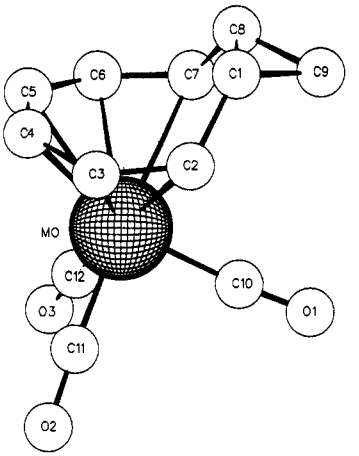


Figure 1. Computer-generated perspective drawing of (bicyclo[6.1.0]nona-2,4,6-triene)tricarbonyl molybdenum. Hydrogens are omitted for clarity.

Table I. Fractional Coordinates and Thermal Parameters for (Bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum[a]

atom	x	y	z	B, Å²
Mo	0.6409 ((1)	0.2500 (0)	0.3546 (2)	4.4 (1)*
C1	0.7542 (11)	0.1798 (16)	−0.0273 (22)	5.2 (4)*
C2	0.7095 (12)	0.1035 (17)	0.1197 (25)	5.7 (5)*
C3	0.6149 (13)	0.0905 (23)	0.1329 (26)	6.2 (6)*
C4	0.5457 (11)	0.1842 (18)	0.1086 (24)	5.3 (4)*
C9	0.8387 (19)	0.2500 (0)	0.0123 (39)	5.9 (7)*
C10	0.7602 (13)	0.2500 (0)	0.4729 (28)	4.4 (5)*
O1	0.8316 (13)	0.2500 (0)	0.5308 (25)	6.7 (5)*
C11	0.5957 (13)	0.1287 (17)	0.5363 (25)	5.9 (5)*
O2	0.5699 (10)	0.0603 (17)	0.6584 (19)	7.7 (4)*
H1	0.7327	0.1114	−0.1211	6.0
H2	0.7524	0.0605	0.2167	6.6
H3	0.5896	−0.0001	0.1643	7.2
H4	0.4809	0.1463	0.0848	6.2
H9	0.8943	0.2500	−0.0808	7.0
H9	0.8674	0.2500	0.1426	7.0

[a] Standard deviations of the least significant figures are given in parentheses. The isotropic equivalent thermal parameter is given for anisotropic atoms (denoted by an asterisk).

Table II. Interatomic Distances (Å) for (Bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum[a]

Mo–C2	2.482 (18)	Mo–C11	1.932 (18)	C2–C3	1.353 (25)
Mo–C3	2.338 (22)	C1–C1*	1.463 (23)	C3–C4	1.396 (27)
Mo–C4	2.336 (17)	C1–C2	1.471 (24)	C4–C4*	1.370 (26)
Mo–C4*	2.336 (17)	C1–C9	1.433 (28)	C10–O1	1.096 (27)
Mo–C10	1.896 (19)	C1*–C9	1.433 (28)	C11–O2	1.192 (24)

[a] The standard deviation of the least significant figure of each distance is given in parentheses.

was equal at the chemically distinct positions (C3/C4 vs. C7/C8) within experimental error (estimated to be approximately 0.8 percentage points). Resubmission of the product to the reaction conditions did not cause any detectable label scrambling.

Starting material recovered from partial reaction (105.0 min at 125.9 °C) had 171.4% of the deuterium at C1/C8, 26.6% at C2/C7, and 2.4% at C3/C6. No deuterium could be detected at C4/C5.

At this stage of the investigation the authors were made aware of unpublished results[8] showing, by X-ray crystallography, that the tungsten tricarbonyl complex of bicyclo[6.1.0]nona-2,4,6-triene did not have the structure proposed by Grimme for the molybdenum complex but rather had the hydrocarbon ligand coordinated with the

(4) Salzer, A. *J. Organomet. Chem.* **1976**, *117*, 245.
(5) Salzer, A. *J. Organomet. Chem.* **1976**, *107*, 79.
(6) Paquette, L. A.; Micheli, R. P.; Photis, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 7911.
(7) The quoted figures are slightly different from those reported in the communication on this work (Liotta, F. J., Jr.; Carpenter, B. K. *J. Am. Chem. Soc.* **1985**, *107*, 6426) because extra data have been gathered in the interim. The figures are corrected for incomplete deuteriation and for contamination by bicyclo[6.1.0]nonatriene labeled at C2/C7. Typical deuterium incorporation was 87%, typical contamination by the C2/C7-labeled material was 2%.

(8) We thank Professor Donald Darensbourg for sharing his results and Professor Maurice Brookhart for making us aware of their existence.

Scheme III. Synthetic Route to Bicyclo[6.1.0]nona-2,4,6-triene-*1,8-d*$_2$

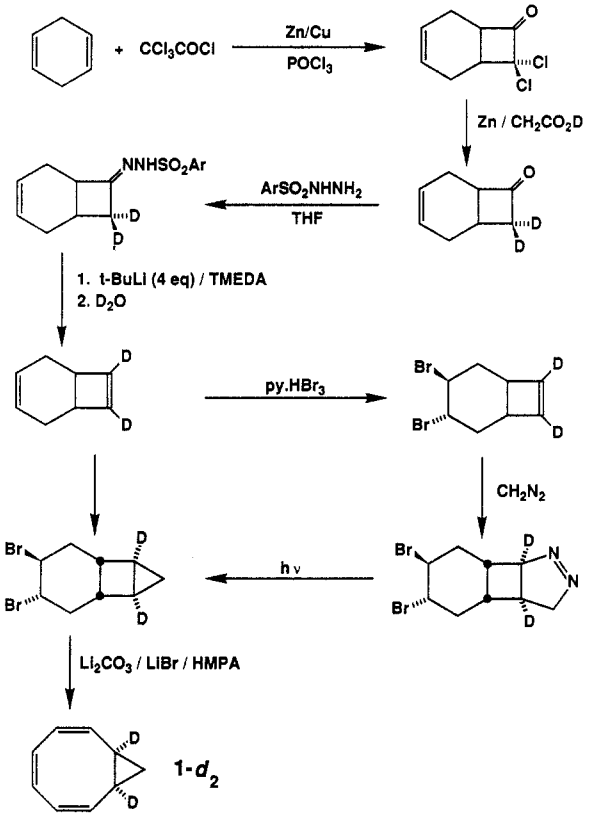


Table III. Interatomic Angles (deg) for (Bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum[a]

C2–Mo–C3	32.4 (6)	C2–Mo–C4	61.7 (6)
C2–Mo–C4*	83.5 (6)	C2–Mo–C10	87.6 (6)
C2–Mo–C11	101.1 (7)	C3–Mo–C4	34.8 (7)
C3–Mo–C4*	66.1 (7)	C3–Mo–C10	116.7 (6)
C3–Mo–C11	87.1 (7)	C4–Mo–C4*	34.1 (6)
C4–Mo–C10	149.3 (6)	C4–Mo–C11	97.7 (7)
C4*–Mo–C10	149.3 (6)	C4*–Mo–C11	121.2 (7)
C10–Mo–C11	89.4 (7)	C1*–C1–C2	122.7 (14)
C1*–C1–C9	59.3 (10)	C2–C1–C9	119.5 (16)
C1–C1*–C9	59.3 (10)	Mo–C2–C1	109.4 (11)
Mo–C2–C3	67.9 (12)	C1–C2–C3	122.3 (17)
Mo–C3–C2	79.6 (12)	Mo–C3–C4	72.5 (12)
C2–C3–C4	128.2 (20)	Mo–C4–C3	72.7 (11)
Mo–C4–C4*	72.9 (10)	C3–C4–C4*	134.4 (16)
Mo–C4*–C4	72.9 (10)	C1–C9–C1*	61.4 (14)
Mo–C10–O1	175.6 (19)	Mo–C11–O2	175.1 (16)

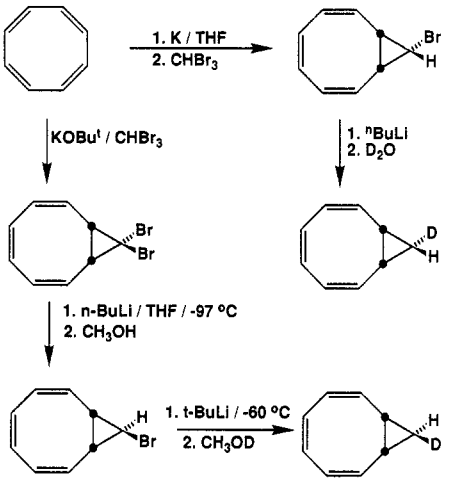
[a] The standard deviation of the least significant figure of each angle is given in parentheses.

cyclopropane ring syn to the metal. Accordingly, an X-ray diffraction experiment was undertaken on the molybdenum compound. Details are given in the Experimental Section.

As shown in the computer-generated perspective drawing (Figure 1), the molybdenum complex also has the cyclopropane unit syn to the metal. The fractional coordinates, interatomic distances, and interatomic angles for the complex are given in Tables I, II, and III, respectively. The fact that the stereochemistry is different from that originally assumed is obviously of profound importance to the mechanism of the thermal rearrangement.

The kinetics of rearrangement of (bicyclo[6.1.0]nonatriene)tricarbonylmolybdenum were investigated. The reaction rate was found to be first order, with activation parameters $\Delta H^{\ddagger} = 27.69 \pm 0.02$ kcal/mol and $\Delta S^{\ddagger} = -7.8 \pm 0.4$ cal/(mol K) between 72.9 and 125.6 °C in cyclohexane solution.

Scheme IV. Synthetic Routes to Bicyclo[6.1.0]nona-2,4,6-triene-*endo*-9-*d* and -*exo*-9-*d*



In order to study the stereochemistry of the rearrangement at the migrating carbon, (bicyclo[6.1.0]nonatriene)tricarbonylmolybdenum labeled stereoselectively at C9 was prepared, as shown in Scheme IV. The individual stereoisomers were converted to the corresponding molybdenum tricarbonyl complexes, and the rearrangement was carried out as before. Recovery of starting material from partial reaction showed that epimerization was occurring and, furthermore, that the rate of the epimerization depended on the concentration of the complex. With use of 1-*9-d* that was 98.4% endo and 1.6% exo, a plot of the retention:inversion ratio in the product vs. the concentration of the starting complex was made over a range of 11–45 mM. The plot was linear and had an intercept corresponding to 1.6 ± 0.8% inversion at zero concentration, showing that the rearrangement occurred with complete retention of configuration. A similar plot for the rearrangement of 1-d_2 revealed no concentration dependence on the label position. No isotope effect could be detected on the rate of rearrangement of any of the labeled complexes.

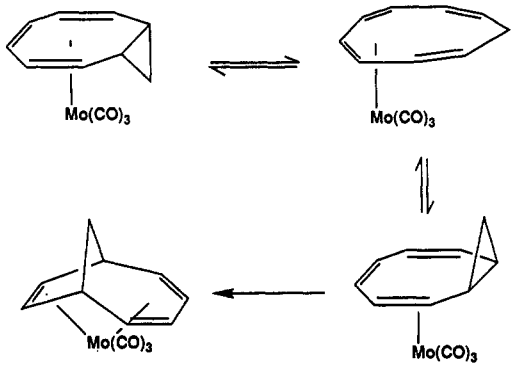
The rearrangements of the chromium tricarbonyl and tungsten tricarbonyl complexes of bicyclo[6.1.0]nonatriene were investigated. At 111.1 °C the relative rate constants for rearrangement were $k_{Cr}/k_{Mo} = 5.9$ and $k_{Mo}/k_{W} = 2.13$. Rearrangement of the chromium and tungsten complexes of 1-d_2 revealed qualitatively the same label distribution in the product as was observed for the molybdenum compound.

Discussion. Before an analysis of specific mechanisms for the rearrangement of (bicyclo[6.1.0]nonatriene)tricarbonylmolybdenum is begun, a few general points can be made. The conversion of free bicyclo[6.1.0]nonatriene to *cis*- and *trans*-8,9-dihydroindenes occurs with a rate constant greater than that for rearrangement of the complex. Since no dihydroindenes were detected and since dihydroindenes do not give the observed product under the reaction conditions, one can conclude with confidence that formation of the bicyclo[4.2.1]nonatriene must be occurring within the coordination sphere of the metal.

A second general observation is that the negative activation entropy determined for the rearrangement seems inconsistent with loss of a CO before or during the rate-determining step of the reaction, particularly given that the kinetics were determined in a noncoordinating solvent (cyclohexane).

The discovery that the complexation of bicyclo[6.1.0]-nona-2,4,6-triene occurs with the cyclopropane ring syn to the metal is of obvious significance to the mechanism of

Scheme V. Hypothetical Mechanism for Unimolecular Syn–Anti Isomerization and Rearrangement of (Bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum

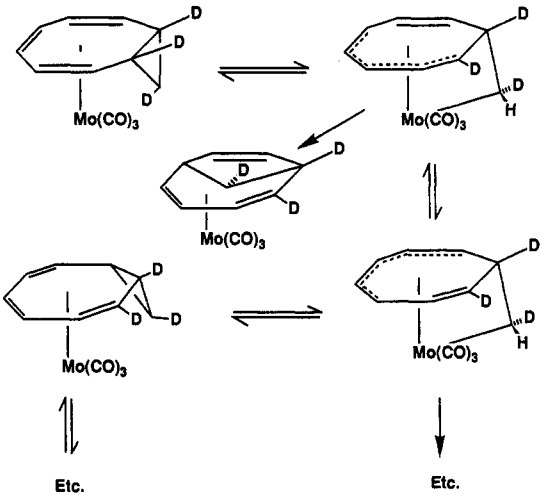


rearrangement of the complex. If the sigmatropic shift ([1,3] or [1,5]) of the methylene bridge occurred from this configuration, the product bicyclo[4.2.1]nonatriene complex would be formed with an exo $M(CO)_3$ moiety which would be incapable of simultaneous coordination to the three double bonds of the hydrocarbon.

The smallest perturbation of the originally proposed mechanism needed to fit the new facts would be to invoke syn–anti isomerization of the starting complex prior to the rearrangement. Such an isomerization could not occur by ligand exchange because the kinetic data show first-order kinetics for the rearrangement. On the other hand the concentration-dependent epimerization of the complexes of 1-*9-d* probably does involve ligand exchange, with the epimerization occurring in the free hydrocarbon. The data of Lewis and Brookhart[9] can be used to show that epimerization of free bicyclo[6.1.0]nonatriene would be very fast under the conditions used for rearrangement of the complexes.

A plausible mechanism that would allow syn–anti isomerization of the starting complex, while still showing overall first-order kinetics for the rearrangement, is shown in Scheme V. The intermediacy of a cyclononatetraene complex is well-precedented in the reaction of bicyclo-[6.1.0]nonatriene with iron carbonyls.[10] A [1,5] sigmatropic shift with *inversion* of configuration at the migrating carbon would explain most of the label distribution in the products observed from 1-d_2 and 1-*9-d*. The inversion of configuration during the migration would be necessary to explain the overall retention of stereochemistry at C9 since the epimerization also corresponds to a formal inversion at this center. The label scrambling in the starting material would be sufficient to explain the appearance of the small amounts of deuterium at C3/C4 and C7/C8 in the product from 1-d_2, but the mechanism of Scheme V does not explain how this isomerization of the starting material occurs. Label scrambling by hydrogen migration in the cyclononatetraene complex can be ruled out because this would allow deuterium to migrate from C9 to other carbons of the ring, an event which experiment shows does not occur. Attempts to prepare *anti*-(bicyclo[6.1.0]nonatriene)tricarbonylmolybdenum by cyclopropanation of (η^6-cyclooctatetraene)tricarbonylmolybdenum were unsuccessful, and so its plausibility as an intermediate in the rearrangement could not be checked. The observation that label scrambling apparently occurs within the starting material while the cyclopropane ring is syn to the metal

Scheme VI. Part of a Hypothetical Mechanism for Competitive Label Scrambling and Skeletal Rearrangement in (Bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum



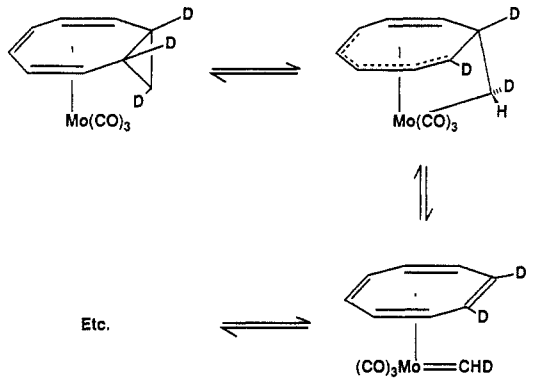
shows that syn–anti isomerization is not a prerequisite for rearrangement.[11] Thus while the data presented here do not rule out the mechanism of Scheme V, it seems unnecessarily complex to propose that syn–anti isomerization is required for the formal [1,5] shift but not for the label scrambling in the starting material, especially when both processes would appear to involve cleavage of the C1–C9 bond.

An alternative mechanism that, at first sight, would appear to be capable of explaining both the scrambling of the deuterium in the starting material and the label distribution in the product is shown in Scheme VI. In this mechanism, oxidative addition of the C1–C9 bond to the metal results in an intermediate that can give the observed product by reductive elimination to the opposite end of the pentadienyl moiety or can undergo a haptotropic shift (degenerate in the absence of labels) and reversion to starting material. The bicyclo[4.2.1]nonatriene would be formed initially with *exo*-η^4-coordination of the metal, but this could presumably revert easily to the final *endo*-η^2,η^4-coordination by ligand exchange. In fact, a control experiment showed that even in the final complex, exchange of the coordinated hydrocarbon with free, labeled bicyclo[4.2.1]nonatriene was very facile under the conditions of the rearrangement reaction. The problem with the mechanism in Scheme VI is that it does not correctly describe the stereochemistry at C9 of degenerate rearrangement in the starting material. As pointed out in the results section, the formation of the final product occurs with complete retention of stereochemistry at C9, *despite the fact the degenerate rearrangement of the starting material is occurring in competition.* This means that the label scrambling reaction in the starting complex, a formal [1,7] shift, must occur with complete inversion at C9. (There is an unfortunate potential confusion in the stereochemical nomenclature here. In the [1,7] shift *inversion* at C9 keeps a label either exo or endo, whereas *retention* at C9 interconverts exo and endo sites with each migration.) Since the formation of the intermediate from oxidative addition, its subsequent haptotropic shift, and reductive elimination back to the bicyclo[6.1.0]nonatriene must be subject to the rules of microscopic reversibility,

(9) Lewis, C. P.; Brookhart, M. *J. Am. Chem. Soc.* **1975**, *97*, 651.
(10) (a) Reardon, E. J.; Brookhart, M. *J. Am. Chem. Soc.* **1973**, *95*, 4311. (b) Deganello, G.; Maltz, H.; Kozarich, J. *J. Organomet. Chem.* **1973**, *60*, 323. (c) Toniolo, L.; Deganello, G. *Ibid.* **1974**, *74*, 255.

(11) In principle label scrambling in the starting complex *could* be preceded by syn–anti isomerization, but since none of the anti complex could be detected at any time during the reaction, this would require that the syn complex be strongly favored at equilibrium, which seems implausible on steric grounds.

Scheme VII. Part of a Hypothetical Mechanism for Competitive Label Scrambling and Skeletal Rearrangement in (Bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum via a Cyclooctatetraene–Methylene Complex



this process cannot occur with net inversion regardless of the stereochemistry of the individual steps. At most one could observe 50% retention and 50% inversion.

The problem of stereochemistry at C9 could be overcome if the migrating methylene became completely disconnected from the ring to give a (η^4-cyclooctatetraene)-methylene complex (Scheme VII), but then the appearance of labels in the eight-membered ring would not be described properly. Thus the complex of 1-d_2 would give an alkylidene intermediate that should revert to the starting structure either with complete label scrambling in the eight-membered ring (if haptotropic migration in the alkylidene complex were fast with respect to return to starting material) or with label appearing at C3 and C4 at equal rates (if haptotropic migration were slow). Neither fits the observation of deuterium appearing faster at C3 than at C4 and faster at C4 than at C5.

The only mechanism that the authors can think of that fits the stereochemistry of the degenerate rearrangement is a single-step [1,7] sigmatropic migration without direct involvement of the metal in C–C bond cleavage. Such a reaction would be thermally allowed if it occurred with inversion at C9 and is, in fact, known for substituted bicyclo[6.1.0]nonatrienes.[12] Again, arguing on grounds of mechanistic economy, if the [1,7] shift occurs without involvement of the metal, it seems unnecessary to involve the metal for the [1,5] shift, which breaks the same C–C bond. The fact that the rates of rearrangement of chromium, molybdenum, and tungsten complexes are so similar is consistent with this picture. Also supportive is the fact that the [1,5] shift occurs in certain substituted bicyclo-[6.1.0]nonatrienes, although with a slight preference for inversion at C9 in the one example where the stereochemistry was studied.[13]

If the mechanism favored by the authors is correct, then the interesting conclusion is that the metals used in this study change the course of the thermal chemistry of bicyclo[6.1.0]nonatriene not by making available new reaction pathways but by selectively inhibiting the epimerization and conversion to dihydroindenes observed for the free hydrocarbon.

Synthesis and Structure of (9-Halobicyclo[6.1.0]nonatriene)tricarbonylmolybdenum Complexes

Treatment of (diglyme)tricarbonylmolybdenum with *exo*-9-bromo-, *endo*-9-bromo-, 9,9-dibromo-, *exo*-9-chloro-, or *endo*-9-chlorobicyclo[6.1.0]nona-2,4,6-triene gave the corresponding molybdenum tricarbonyl complex of each organic ligand.

Table IV. ^{13}C Chemical Shifts for (9-Halobicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum Complexes in C_6D_6

R_{exo}	R_{endo}	δ_{C2-C7}			$\delta_{C1/C8}$	δ_{C9}
H	H	101.4	97.0	88.5	19.2	12.6
Cl	H	101.1	96.0	82.5	30.6	37.3
H	Cl (major)	100.2	97.8	82.0	26.1	36.7
	Cl (minor)	131.2	102.8	98.6	18.1	52.7
Br	H	101.1	95.9	82.8	30.8	23.3
H	Br (major)	131.3	101.9	99.9	18.2	43.7
	Br (minor)	99.0	97.8	84.4	26.0/27.0	27.0/26.0
Br	Br (major)	131.5	98.6	96.7	31.3	44.2
	Br (minor)	100.1	96.1	82.5	40.0	31.3

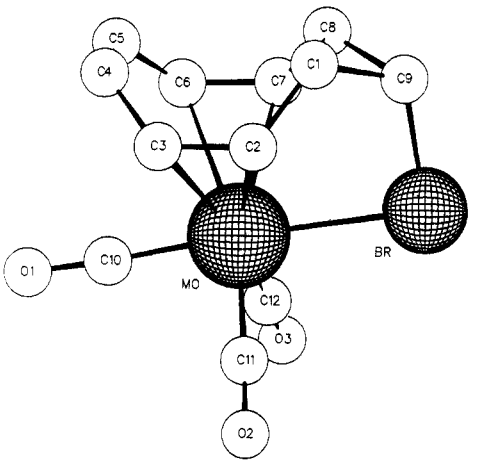


Figure 2. Computer-generated perspective drawing of (*endo*-9-bromobicyclo[6.1.0]nona-2,4,6-triene)tricarbonyl molybdenum. Hydrogens are omitted.

For three of the five complexes, ^1H and ^{13}C NMR spectroscopy indicated formation of two apparently isomeric compounds. The ^{13}C chemical shifts are listed in Table IV.

In each of the complexes containing an endo halogen one of the compounds formed had spectral characteristics similar to those for all the other bicyclo[6.1.0]nonatriene complexes, while the other showed a single anomalously low-field ^{13}C NMR resonance, similar in position to that observed for an olefinic carbon in uncomplexed bicyclo-[6.1.0]nonatriene. This observation suggested that one double bond was not coordinated to the metal in the new complexes; if this were correct, the symmetry of the spectra would demand that it be the 4,5 double bond. Furthermore, since the new complexes were formed only when the ligand had an endo halogen, it seemed reasonable to speculate that the structure was one in which the halogen occupied the coordination site vacated by the olefin.

This speculation was confirmed by X-ray crystallography on the endo 9-bromo complex. A computer-generated perspective drawing of the complex is shown in Figure 2. Fractional coordinates, interatomic distances, and interatomic angles are listed in Tables V, VI, and VII, respectively. Other details of the crystallography are given in the Experimental Section.

The relative concentrations of the isomeric complexes formed from the endo 9-halo ligands were found to be reversibly temperature dependent, showing that they were at equilibrium. The ratios of halogen-coordinated to "normal" complexes at 25 °C were 7.6:1 for the endo 9-bromo, 3.8:1 for the 9,9-dibromo, and 1:3 for the endo 9-chloro ligand. This trend is probably in the direction expected for the size and electron-donating ability of the

(12) Klärner, F.-G. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 832.
(13) Klärner, F.-G. *Tetrahedron Lett.* **1971**, 3611.

Table V. Fractional Coordinates and Thermal Parameters for (*endo*-9-Bromobicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum[a]

atom	x	y	z	B, Å²
Mo	0.8269 (1)	0.2500 (0)	0.9008 (1)	2.1 (0)*
C1	1.1604 (11)	0.1739 (11)	0.8125 (7)	3.0 (3)*
C2	1.0123 (11)	0.1001 (9)	0.8257 (7)	2.6 (2)*
C3	0.9008 (12)	0.1050 (10)	0.7587 (8)	3.1 (3)*
C4	0.9047 (11)	0.1811 (12)	0.6727 (7)	3.3 (3)*
C9	1.2175 (16)	0.2500 (0)	0.8950 (11)	3.0 (4)*
Br	1.0743 (2)	0.2500 (0)	1.0118 (1)	3.5 (0)*
C10	0.6436 (16)	0.2500 (0)	0.8289 (11)	2.9 (4)*
O1	0.5373 (12)	0.2500 (0)	0.7816 (9)	4.2 (3)*
C11	0.7265 (11)	0.1149 (10)	0.9867 (7)	2.9 (3)*
O2	0.6647 (10)	0.0344 (8)	1.0355 (6)	4.6 (2)*
Mo′	0.6092 (1)	0.2500 (0)	1.3713 (1)	2.2 (0)*
C1′	0.2547 (11)	0.1736 (11)	1.3939 (8)	3.1 (3)*
C2′	0.3961 (11)	0.0961 (10)	1.3569 (8)	3.1 (3)*
C3′	0.4614 (12)	0.1010 (10)	1.2656 (7)	3.0 (3)*
C4′	0.4089 (11)	0.1844 (12)	1.1830 (8)	3.6 (3)*
C9′	0.2495 (16)	0.2500 (0)	1.4845 (11)	3.1 (4)*
Br′	0.4410 (2)	0.2500 (0)	1.5486 (1)	3.7 (0)*
C10′	0.7458 (16)	0.2500 (0)	1.2521 (11)	2.8 (4)*
O1′	0.8299 (15)	0.2500 (0)	1.1848 (9)	5.8 (4)*
C11′	0.7534 (12)	0.1179 (11)	1.4136 (7)	3.1 (3)*
O2′	0.8464 (10)	0.0404 (10)	1.4346 (6)	5.0 (3)*
H1	1.2038	0.1009	0.7670	3.4
H2	0.9918	0.0433	0.8874	2.7
H3	0.8051	0.0476	0.7737	3.4
H4	0.9077	0.1325	0.6071	3.7
H9	1.3187	0.2500	0.9280	3.2
H1′	0.1887	0.0998	1.3659	3.4
H2′	0.4461	0.0356	1.4059	2.9
H3′	0.5563	0.0422	1.2505	3.3
H4′	0.3710	0.1363	1.1233	3.9
H9′	0.1763	0.2500	1.5471	3.5

[a] Standard deviations of the least significant figures are given in parentheses. The isotropic equivalent thermal parameter is given for anisotropic atoms (denoted by an asterisk).

Table VI. Interatomic Distances (Å) for (*endo*-9-Bromobicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum[a]

Mo–C2	2.391 (9)	C3–C4	1.405 (15)	C1′–C1′*	1.533 (15)
Mo–C3	2.483 (11)	C4–C4*	1.384 (17)	C1′–C2′	1.517 (14)
Mo–Br	2.734 (2)	C9–Br	1.963 (15)	C1′–C9′	1.460 (17)
Mo–C10	1.941 (15)	C10–O1	1.171 (19)	C1′*–C9′	1.460 (17)
Mo–C11	1.963 (10)	C11–O2	1.159 (13)	C2′–C3′	1.341 (14)
C1–C1*	1.527 (16)	Mo′–C2′	2.439 (10)	C3′–C4′	1.509 (16)
C1–C2	1.491 (13)	Mo′–C3m	2.507 (11)	C4′–C4′*	1.318 (17)
C1–C9	1.483 (17)	Mo′–Br′	2.754 (2)	C9′–Br′	1.946 (15)
C1*–C9	1.483 (17)	Mo′–C10′	1.956 (14)	C10′–O1′	1.140 (18)
C2–C3	1.388 (15)	Mo′–C11′	1.947 (11)	C11′–o2′	1.176 (14)

[a] The standard deviation of the least significant figure of each distance is given in parentheses.

endo halogens. Relatively few cases of organic halogen compounds acting as ligands to transition metals have been reported,[14] and, to the authors' knowledge, in no other case has it been possible to observe the intramolecular competition between a halogen and another ligand.

Pyrolyses of the 9-halo complexes gave several products, with indene being the major and only readily identifiable one in each case. This is consistent with earlier reports on the thermal reactions of 9-substituted (bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum complexes.[5]

Experimental Section

General Techniques. ^{1}H NMR spectra were recorded by using a 60-MHz Hitachi Perkin-Elmer R24B, a 90-MHz Varian EM390, an 80-MHz Varian CFT20, or a 300-MHz Bruker WM300 spectrometer. Proton–proton coupling constants were reported by assuming first-order coupling. ^{13}C NMR spectra were recorded on a JEOL FX90Q spectrometer at 22.49 MHz. Proton-coupled ^{13}C spectra were collected in an off-resonance-decoupling mode, so accurate coupling constants were not obtained. The spectra were referenced to the solvent peak, benzene-d_6 at 128.0 ppm or $CDCl_3$ at 77.0 ppm. ^{2}H NMR spectra were recorded by using a Bruker WM300 spectrometer at 46.07 MHz. The spectra were obtained through the lock channel and were ^{1}H broad-band decoupled where indicated. When long scan times were required, the data were accumulated in several parts and the transformed spectra were added together to minimize peak broadening due to field drift. The spectra were referenced to a small amount of the appropriate deuteriated solvent (for toluene benzene-d_6 was used). Integrals for ^{1}H NMR spectra were calculated from the average of a minimum of five integrations from spectra recorded by using a pulse delay of 5–7T_1. The T_1 relaxation times were determined by using the spin-saturation recovery method.[15] Integrals for ^{2}H NMR spectra were calculated from a minimum of five integrations. In the cases of poor signal to noise ratios the integrals were measured by cutting and weighing the peaks. Pulse delays were not used in collecting ^{2}H NMR spectra since test experiments indicated that they were not necessary.[16]

Infrared (IR) spectra were recorded on either a Beckman IR 8, a Perkin-Elmer 137, or a Perkin-Elmer 681 spectrophotometer and calibrated to the 1601 cm^{-1} absorption of polystyrene film. Unless otherwise indicated NaCl plates or solution cells were used.

Low-resolution mass spectra data were obtained on a Finnigan 3300 mass spectrometer at 70 eV for electron impact (EI) using methane or isobutane chemical ionization (CI). Microanalyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN). Melting points were taken in open capillary tubes in a Thomas-Hoover unimelt capillary melting point apparatus and were not corrected.

Thin-layer chromatography (TLC) plates were plastic backed silica plates (Macherey-Nagel pre-coated SIL G/UV$_{254}$, 0.25 mm, from Brinkmann Instruments). The plates were visualized by phosphomolybdic acid (3% w/w in 2-propanol, dipped and heated

Table VII. Interatomic Angles (deg) for (*endo*-9-Bromobicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum[a]

C2–Mo–C3	33.0 (3)	C2–Mo–Br	72.7 (2)
C2–Mo–C10	109.8 (4)	C2–Mo–C11	94.9 (4)
C3–Mo–Br	105.5 (2)	C3–Mo–C10	77.2 (4)
C3–Mo–C11	98.5 (4)	Br–Mo–C10	176.7 (4)
Br–Mo–C11	90.1 (3)	C10–Mo–C11	87.5 (4)
C1*–C1–C2	119.8 (8)	C1*–Cl–C9	59.0 (6)
C2–C1–C9	120.0 (9)	C1–C1*–C9	59.0 (6)
Mo–C2–C1	107.2 (6)	Mo–C2–C3	77.1 (6)
C1–C2–C3	123.1 (9)	Mo–C3–C2	69.8 (6)
Mo–C3–C4	109.4 (7)	C2–C3–C4	126.9 (9)
C3–C4–C4*	122.9 (10)	C1–C9–C1*	62.0 (9)
C1–C9–Br	113.3 (8)	Cl*–C9–Br	113.3 (8)
Mo–Br–C9	91.6 (4)	Mo–C10–O1	177.0 (13)
Mo–C11–O2	178.2 (9)	C2′–Mo′–C3′	31.4 (3)
C2′–Mo′–Br′	73.1 (2)	C2′–Mo′–C10′	110.9 (4)
C2′–Mo′–C11′	96.2 (4)	C3′–Mo′–Br′	104.4 (2)
C3′–Mo′–C10′	79.9 (4)	C3′–Mo′–C11′	97.9 (4)
Br′–Mo′–C10′	174.7 (4)	Br′–Mo′–C11′	93.0 (3)
C10′–Mo′–C11′	83.2 (4)	C1′*–C1′–C2′	120.8 (8)
C1′*–C1′–C9′	58.3 (7)	C2′–C1′–C9′	122.0 (10)
C1′–C1′*–C9′	58.3 (7)	Mo′–C2′–C1′	104.9 (6)
Mo′–C2′–C3′	77.1 (6)	C1′–C2′–C3′	125.2 (10)
Mo′–C3′–C2′	71.5 (6)	Mo′–C3′–C4′	107.6 (7)
C2′–C3′–C4′	126.3 (9)	C3′–C4′–C4′*	123.7 (10)
C1′–C9′–C1′*	63.4 (9)	C1′–C9′–Br′	114.3 (8)
C1′*–C9′–Br′	114.3 (8)	Mo′–Br′–C9′	91.2 (4)
Mo′–C10′–O1′	177.5 (13)	Mo′–C11′–O2′	176.1 (9)

[a] The standard deviation of the least significant figure of each angle is given in parentheses.

(14) (a) Crabtree, R. H.; Faller, J. W.; Quirk, J. M.; Mella, M. F. *Organometallics* **1982**, *1*, 1361. (b) Crabtree, R. H.; Mella, M. F.; Quirk, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 2913.

(15) McDonald, G. G.; Leigh, J. S. *J. Magn. Reson.* **1973**, *9*, 358.

(16) For a review on ^{2}H NMR see: Mantsch, H. H.; Saito, H.; Smith, I. C. P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 211.

with heat gun) or by ultraviolet light. Preparative thin-layer chromatography was performed on 20 × 20 cm glass plates coated with 1 mm of silica with a fluorescent indicator (from Analtech). Flash chromatography refers to the medium-pressure chromatographic technique developed by Still.[17] Flash chromatography was performed on "silica gel 60 for chromatography" from EM Science (E. Merck).

Analytical packed-column gas chromatography (GC) was performed on a Hewlett-Packard 700 laboratory chromatograph equipped with a Model 240 temperature programmer and a thermal conductivity detector. Peak areas were determined with a Spectra-Physics minigrator. Capillary gas chromatography was performed on a Hewlett-Packard 5880 series gas chromatograph equipped with a 12 m by 0.2 mm i.d. methylsilicone-deactivated Carbowax 20 M column (latter referred to as methylsilicone), flame ionization detector, and a Hewlett-Packard 5880 series GC printer. The hydrogen flow to the detector was 30 mL/min, and the air flow was 400 mL/min. The helium flow was maintained at 1.0 mL/min, and the detector was kept at 250 °C. The injector was heated to 200 °C unless otherwise stated. Preparative gas chromatography was performed on a Aerograph Autoprep Model A-700 chromatograph. The injections were made directly on the appropriate column.

For rearrangement studies and kinetics above 85 °C a Tamson Holland regulated-temperature bath was used, and for those performed below 85 °C a Neslab EX-200 temperature bath was used. The temperature was corrected by using the standard liquid in glass stem correction formula.[18]

Photolysis reactions were performed by using 450-W Canard-Hanovia medium-pressure mercury vapor lamp powered by an Ace Hanovia Model 7830 power supply. A jacketed Pyrex immersion well was used with tap water cooling. The outer cooling jacket, which was part of some of the reaction vessels, was not used.

For organic reactions the removal of solvent refers to the use of a Büchi rotary evaporator at aspirator pressure.

All syringes were Hamilton Series 1000 with Teflon plungers and either a fixed needle or a Teflon lure lock. The syringe pump used was a Sage Instruments Model 341A.

Unless stated otherwise all reactions were performed under an atmosphere of argon or nitrogen. All glassware was dried in an oven and cooled in a desiccator over P_2O_5. The term "drybox" refers to a Vacuum Atmospheres HE-43-2 Dri-Lab with a HE-63-P Pedatrol. All organometallic reaction were performed on a double-manifold vacuum line using argon passed over a column of BASF deoxygenation catalyst (R3-11) and a column of Mallinckrodt Aquasorb. The term "filter frit" refers to the apparatus in Figure 3. Size C refers to a 25–50 μm pore size and D to a 10–20 μm pore size.

All reactions using diazomethane were performed by using glassware with O-ring joints and not ground-glass joints and were conducted in a well-ventilated fume hood behind at least one blast shield.

Solvents and Reagents. All solvents were distilled under an atmosphere of argon or nitrogen from an appropriate drying agent. Anhydrous diethyl ether and absolute ethanol were used without further purification.

Solvents for organometallic reactions were transferred via the vacuum line. THF, diethyl ether, benzene, and toluene were transferred from sodium benzophenone ketyl. Hexane and heptane were transferred from sodium benzophenone ketyl and tetraglyme. Acetonitrile was vacuum transferred from CaH_2.

Molybdenum hexacarbonyl, tungsten hexacarbonyl, and chromium hexacarbonyl were all sublimed at 60 °C under a static vacuum prior to use. Lithium carbonate and lithium bromide were dried for a minimum of week in an oven and stored in a drybox. Pyridinium bromide perbromide was Aldrich technical grade and was recrystallized from acetic acid prior to use. Phosphorus oxychloride was distilled from anhydrous potassium carbonate under nitrogen. Zinc dust was purchased from Fisher Scientific Co. Other brands of zinc dust produced unsatisfactory results.

(17) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(18) West, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 59th ed.; CRC Press: FL, 1978; p D-231.

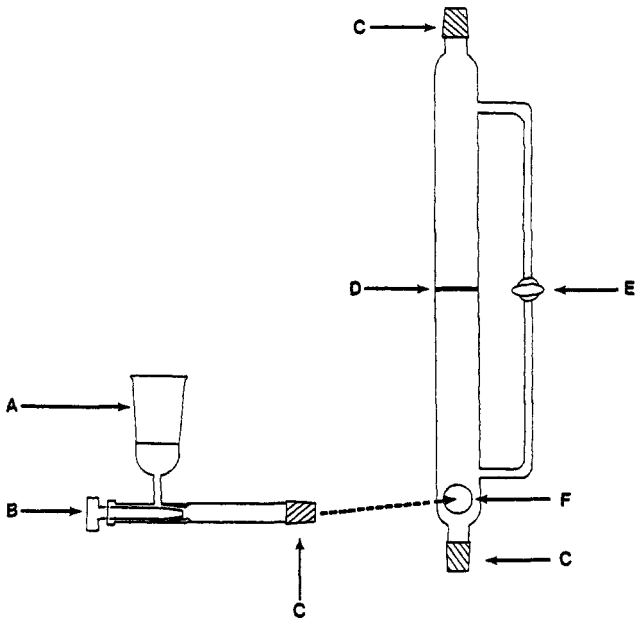


Figure 3. Filter frit used for air-sensitive reactions: A, 24/40 outer joint; B, stopcock; C, 14/20 inner joint; D, fritted disk; E, stopcock; F, 14/20 outer joint.

Preparation of Zinc Copper Couple for Generation of Dichloroketene. The zinc copper couple that was used in the preparation of dichloroketene from trichloroacetyl chloride was prepared from zinc dust and copper sulfate by the method of Krepski and Hassner.[19] After the couple was dried under vacuum, it was weighed and stored in a drybox.

8,8-Dichlorobicyclo[4.2.0]oct-3-en-7-one. A solution of predistilled 1,4-cyclohexadiene (50.0 g, 630.5 mmol) in 500 mL of anhydrous diethyl ether was added under an atmosphere of argon to zinc opper couple (above) (30.0 g) in a dry 1000-mL round-bottomed flask fitted with a reflux condenser and a mechanical stirrer. A second solution containing freshly distilled trichloroacetyl chloride (56.0 g, 308 mmol) and phosphorus oxychloride (47.2 g, 308 mmol), freshly distilled from anhydrous potassium carbonate, in 175 mL of anhydrous ether was prepared in a dry flask. The second solution was added over 10 h with a syringe pump to the first solution at reflux. After the addition was complete, the solution was refluxed under an atmosphere of argon for an additional 36 h. The solution was cooled to room temperature and filtered through a Celite pad. The pad was washed with 200 mL of diethyl ether. The ether solutions were combined and concentrated to approximately 200 mL under reduced pressure. To this solution was added 200 mL of hexane, and the resulting solution was stirred 30 min. The resulting two phases were separated, and the non-hexane soluble phase was treated again with 200 mL of 1:1 hexane/diethyl ether. The combined organic phases were washed five times with 100 mL of water, followed by 100 mL of a saturated sodium bicarbonate solution, and finally with 100 mL of a saturated sodium chloride solution. The solution was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The product was distilled at 0.1 mmHg and 70–78 °C to give 8,8-dichlorobicyclo-[4.2.0]oct-3-en-7-one (30.8 g, 162 mmol) in a yield of 52.7%: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.82 (m, 2 H), 4.00 (ddd, J = 2.5, 7.1, 10.7 Hz, 1 H), 3.29 (ddd, J = 2.3, 7.9, 10.7 Hz, 1 H), 2.56 (ddd, J = 2.1, 4.8, 19 Hz, 1 H), 2.49 (ddd, J = 2.4, 5.1, 19 Hz, 1 H), 2.31 (ddm, J = 7.9, 17.5 Hz, 1 H), 2.09 (ddm, J = 7.1, 17.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 198.0 (s), 126.9 (d), 126.0 (d), 88.3 (s), 53.5 (d), 44.9 (d), 22.8 (t), 21.0 (t); IR (neat, cm^{-1}) 3050 (m), 2980 (m), 1800 (s), 740 (m); MS (EI) m/z (relative intensity) 192 (0.4), 191 (0.5), 190 (1.9), 189 (0.8), 188 (M^+, 2.8), 165 (0.4), 164 (0.9), 163 (2.3), 62 (4.6), 161 (4.7), 160 (6.7), 150 (1.3), 149 (4.1), 148 (6.8), 147 (8.4), 146 (9.7), 145 (4.5), 128 (10.3), 127 (10.0), 126 (34.0), 125 (24.0), 114 (8.6), 113 (7.5), 112 (27.8), 111 (16.8), 92 (3.8), 91 (11.9), 90 (100).

(19) Krepski, L. R.; Hassner, A. *J. Org. Chem.* **1978**, *43*, 2879.

Bicyclo[4.2.0]oct-3-en-7-one. A suspension of zinc dust (23.8 g, 364 mmol) in 45 mL of acetic acid was prepared in a round-bottomed flask equipped with a mechanical stirrer. To this was added a solution of 8,8-dichlorobicyclo[4.2.0]oct-3-en-7-one (10.5 g, 55.0 mmol) in 15 mL of acetic acid dropwise over 45 min. The reaction was exothermic. The suspension was then warmed in a 75–80 °C oil bath for an additional 2 h. The suspension was cooled to room temperature and diluted with 225 mL of diethyl ether. The resulting solution was filtered and washed twice with 100 mL of water, followed by four washes with 75 mL of saturated $NaHCO_3$, and finally with 100 mL of brine. The washes were checked with pH paper to be sure that all of the acid had been neutralized. (Traces of acid result in decomposition of the product during the distillation.) The ether solution was dried over $MgSO_4$. The solution was filtered and the ether removed. The product was distilled at 18–24 mmHg, and the fraction that distilled between 76 and 80 °C was collected. The product bicyclo-[4.2.0]oct-3-en-7-one (5.43 g, 44.5 mmol) was isolated in a yield of 81.0%: ^1H NMR ($CDCl_3$, 300 MHz) δ 5.855 (d, J = 2.7 Hz, 1 H), 5.845 (d, J = 2.7 Hz, 1 H), 3.42 (m, 1 H), 3.20 (ddd, J = 3.9, 9.2, 17.9 Hz, 1 H), 2.77 (dddm, J = 2.7, 9.2, 12.0 Hz, 1 H), 2.52 (ddd, J = 3.1, 5.3, 17.9 Hz, 1 H), 2.32 (m, 2 H), 2.10 (m, 2 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 212.9 (s), 127.4 (d), 126.3 (d), 56.5 (d), 52.0 (t), 26.5 (t), 21.9 (t), 21.7 (d); IR (neat, cm^{-1}) 3050 (m), 2930 (m), 2850 (m), 1785 (s); MS (EI) m/z (relative intensity) 124 (0.2), 123 (0.9), 122 (M^+, 5.2), 121 (2.7), 108 (9.2), 107 (2.9), 106 (1.1), 105 (0.7), 104 (3.5), 94 (0.6), 93 (1.9), 92 (1.3), 91 (6.4), 82 (0.5), 81 (4.4), 80 (52.5), 79 (100), 78 (29.3), 77 (30.0). Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.93; H, 8.12.

Bicyclo[4.2.0]oct-3-en-7-one-*8,8*-d_2. A suspension of zinc dust (86.67 g, 1.33 mol) in 139 mL of acetic acid-*d* was prepared in a dry flask equipped with a mechanical stirrer.[20] To this stirring suspension at room temperature was added a solution of 8,8-dichlorobicyclo[4.2.0]oct-3-en-7-one (36.1 g, 189 mmol) in 36 mL of acetic acid-*d* dropwise over 30 min under argon. The suspension was then heated in a 76–78 °C oil bath for 60 min more. The suspension was cooled to room temperature, diluted with 800 mL of diethyl ether, and filtered through a glass wool plug. This solution was stirred with 300 mL of water. Sodium carbonate powder was added in small portions to this stirring mixture until all the acetic acid was neutralized. The two phases were separated, and the organic phase was washed with 100 mL of saturated sodium chloride solution. The ether solution was dried over magnesium sulfate and filtered. After the solvent was removed under reduced pressure, the product was distilled at 0.15 mmHg and 35–39 °C to give bicyclo[4.2.0]oct-3-en-7-one-*8,8*-d_2 (20.56 g, 168.2 mmol) in a yield of 89.0%. The deuterium incorporation was normally 94–97% by ^1H NMR: ^1H NMR ($CDCl_3$, 300 MHz): δ 5.85 (bdd, J = 2.8, 2.8 Hz, 2 H), 3.42 (bddd, J = 2.0, 8.9, 8.9 Hz, 1 H), 2.76 (bt, 1 H), 2.33 (m, 2 H), 2.03 (m, 2 H); $^2H\{^1H\}$ NMR ($CHCl_3$, 46 MHz) δ 3.05 (s, 1 D), 2.30 (s, 1 D), 3.23 (trace); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22.5 MHz): δ 212.7, 127.0, 126.2, 52.2, 51.3 (m), 26.0, 21.6, 21.1; IR (neat, cm^{-1}) 3050 (m), 2920 (m), 2830 (m), 2180 (w), 1760 (s), 1430 (m), 1097 (m); MS (EI) m/z (relative intensity) 126 (0.2), 125 (0.9), 124 (M^+, 2.8), 123 (1.6), 122 (0.2), 108 (0.6), 107 (2.6), 106 (3.3), 105 (1.3), 97 (0.7), 96 (1.7), 95 (3.3), 94 (2.9), 93 (4.9), 92 (4.0), 91 (1.4), 83 (0.8), 82 (4.6), 81 (22.4), 80 (66.8), 79 (100), 78 (42.3), 77 (30.2).

2,4,6-Triisopropylbenzenesulfonyl Chloride. 2,4,6-Triisopropylbenzenesulfonyl chloride [mp 94–96 °C (lit. mp 96–97 °C)] was prepared from 1,3,5-triisopropylbenzene and chlorosulfonic acid by using the procedure of Lohrmann and Khorana.[21]

2,4,6-Triisopropylbenzenesulfonyl Hydrazine. 2,4,6-Triisopropylbenzenesulfonyl hydrazine was prepared from 2,4,6-triisopropylbenzenesulfonyl chloride and hydrazine monohydrate according to the procedure of Cusack, Reese, Risius, and Roozpeikar.[22] The white fluffy powder [mp 119.5–120.5 °C (lit. mp 118–120 °C)] was stored in the dark in the freezer. If some decomposition had taken place during storage, the compound was purified by the literature method: ^1H NMR ($CDCl_3$, 60 MHz) δ 7.18 (s, 2 H), 4.22 (sep, J = 7 Hz, 2 H), 2.92 (sep, J = 7 Hz, 1 H), 1.28 (d, J = 7 Hz, 12 H), 1.25 (d, J = 7 Hz, 6 H).

Bicyclo[4.2.0]oct-3-en-7-one 2,4,6-Triisopropylbenzenesulfonyl Hydrazone. A solution of bicyclo[4.2.0]oct-3-en-7-one (113 mg, 0.92 mmol) and 2,4,6-triisopropylbenzenesulfonyl hydrazine (303 mg, 1.02 mmol) was prepared in 0.8 mL of dry THF. After being stirred for 2.5 h at room temperature, the solution was stored in a freezer overnight. The THF was removed, leaving a white oily solid, which was purified by flash chromatography on a 2 cm × 12 cm silica column using 3:1 hexane/ethyl acetate. The fractions containing product (R_f 0.38, 3:1 hexane/ethyl acetate) were combined. After the solvent was removed, the product (365 mg, 92 mmol) was obtained in a yield of 99%: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.23 (s, 2 H), 7.11 (s, 1 H), 5.82 (m, 1 H), 5.74 (m, 1 H), 4.27 (sep, J = 6.7 Hz, 2 H), 3.45 (m, 1 H), 3.02 (sep, J = 6.9 Hz, 1 H), 2.90 (m, 1 H), 2.78 (m, 1 H), 2.03–2.35 (m, 5 H), 1.37 (d, J = 6.9 Hz, 6 H), 1.35 (d, J = 6.7 Hz, 12 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 161.6 (s), 153.0 (s), 151.1 (s), 131.3 (s), 128.1 (d), 126.1 (d), 123.5 (d), 43.7 (d), 35.9 (t), 34.1 (d), 29.7 (d), 26.7 (t), 25.3 (t), 24.7 (q), 23.5 (q); IR (thin film, cm^{-1}) 3220 (m), 3040 (w), 2940 (s), 2860 (m), 1760 (w), 1670 (w), 1590 (m), 1550 (w), 1448 (m), 1420 (m), 1375 (m), 1335 (m), 1315 (m), 1163 (s), 1075 (m), 1020 (m), 903 (m). Anal. Calcd for $C_{23}H_{34}O_2N_2S$: C, 68.62; H, 8.51; N, 6.96; S, 7.96. Found: C, 68.66; H, 8.75; N, 6.73; S, 8.00.

Bicyclo[4.2.0]oct-3-en-7-one-*8,8*-d_2 2,4,6-Triisopropylbenzenesulfonyl Hydrazone. A 250-mL round-bottomed flask was charged with 2,4,6-triisopropylbenzenesulfonyl hydrazine (47.00 g, 158 mmol) and bicyclo[4.2.0]oct-3-one-*8,8*-d_2 (14.68 g, 118.4 mmol) in 175 mL of dry THF. The solution was stirred at room temperature for 6 h under argon. The THF was removed, and the resulting white solid was ground to a fine powder and triturated twice with 25 mL of methanol. After removal of the methanol by filtration, the product was dried under vacuum to give the hydrazone (46.36 g, 115 mmol) in a yield of 96.9% (mp 120–123 °C dec). TLC in 19:1 $CHCl_3$/methanol on silica showed the product (R_f 0.68) and just a trace of the hydrazine: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.50 (s, 1 H), 7.23 (s, 2 H), 5.82 (m, 1 H), 5.74 (m, 1 H), 4.27 (sep, J = 6.7 Hz, 2 H), 3.45 (m, 1 H), 3.02 (sep, J = 6.9 Hz, 1 H), 2.90 (trace, <1 H), 2.78 (m, 1 H), 2.03–2.35 (m, 4.1 H), 1.37 (d, J = 6.9 Hz, 6 H), 1.35 (d, J = 6.7 Hz, 12 H); $^2H\{^1H\}$ NMR ($CHCl_3$, 46 MHz) δ 2.85 (vbs), 2.22 (vbs); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 22.5 MHz) δ 161.7, 153.0, 151.2, 131.3, 128.2, 126.1, 123.7, 43.8, 35.8 (m, trace), 34.1, 29.7, 26.6, 25.1, 25.0, 24.7, 23.5; IR (thin film, cm^{-1}) 3220 (m), 2960 (s), 1760 (w), 1675 (w), 1600 (m), 1540 (w), 1460 (m), 1425 (m), 1380 (w), 1360 (w), 1330 (m), 1160 (s), 1010 (w), 880 (w).

Bicyclo[4.2.0]octa-3,7-diene. A suspension of bicyclo-[4.2.0]oct-3-en-7-one 2,4,6-triisopropylbenzenesulfonyl hydrazone (9.74 g, 24.4 mmol) in 50 mL of freshly distilled TMEDA and 15 mL of dry pentane was prepared in a 250-mL round-bottomed flask equipped with a pressure-equalizing addition funnel and a gas inlet. This suspension was cooled in a −50 °C bath. To this cooled suspension was added a 1.8 M solution of *tert*-butyllithium solution in pentane (60 mL (128 mmol) dropwise over 20 min under argon. The red solution was stirred in a −50 to −60 °C bath for 3 h. The solution was then warmed to 0 °C in an ice bath. As the temperature of the solution approached 0 °C, N_2 was evolved. When the N_2 evolution stopped, in approximately 15 min, the solution was quenched by the dropwise addition of 5 mL of water. The solution was diluted with 100 mL of water and 125 mL of pentane. The dilution was performed slowly to allow any 2-methylpropane to boil off. The layers were separated, and the aqueous layer was extracted once with 100 mL and twice with 50 mL of pentane. The combined pentane solutions were washed four times with 75 mL of water. The organic layer was then combined with 75 mL of water and cooled in an ice bath. To this stirring mixture was slowly added concentrated HCl until pH 2 was obtained. The organic layer was then washed with 100 mL of water, followed by 75 mL of saturated $NaHCO_3$. The pentane solution was then dried over $MgSO_4$ and filtered. The pentane was then removed by distillation through a 18-cm Vigreux column. The product was then distilled through a 10-cm Vigreux column under N_2. The fraction which distilled at 120–129 °C was collected. GC on a 3% methylsilicone capillary column at 50 °C (He

(20) It is important that a good quality zinc dust be used; otherwise the slow reaction results in contamination by d_3 material, due to a competitive exchange reaction.

(21) Lohrmann, R.; Khorana, H. G. *J. Am. Chem. Soc.* **1966**, *88*, 829.

(22) Cusack, N. J.; Reese, C. B.; Risius, A. C.; Roozpeikar, B. *Tetrahedron* **1976**, *32*, 2157.

pressure 40 psi, detector 250 °C, injector 200 °C) showed a major peak, retention time of 3.27 min, which corresponded to the product, and several other smaller peaks. A total of 1.92 g of material was collected, which was 83% pure (GC), in a yield of 62%. ^{1}H NMR corresponded to the desired product, bicyclo-[4.2.0]octa-3,7-diene, and traces of other material, including some 2,2,3,3-tetramethylbutane: ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 137.3 (d), 125.4 (d), 40.4 (d), 26.3 (t); IR (neat, cm^{-1}) 3050 (m), 2950 (m), 1785 (m), 1645 (m), 1435 (m), 1305 (m), 1000 (m), 875 (m); MS (EI) *m/z* (relative intensity) 107 (1.8), 106 (M^+, 21.3), 105 (21.6), 92 (7.4), 91 (95.5), 79 (45.7), 78 (100), 77 (35.2), 65 (15.6), 52 (20.9), 51 (25.7), 50 (13.4).

Bicyclo[4.2.0]octa-3,7-diene-7,8-d_2. A suspension of bicyclo[4.2.0]oct-3-en-7-one-8,8-d_2 2,4,6-triisopropylbenzenesulfonyl hydrazone (54.55 g, 135 mmol) in 650 mL of freshly distilled TMEDA and 150 mL of dry pentane was prepared under an atmosphere of argon in a 2-L round-bottomed flask equipped with pressure-equalizing addition funnel and a gas inlet. The solution was cooled in a −60 to −65 °C bath. To this suspension was added a 2.0 M *tert*-butyllithium solution in pentane (270 mL, 540 mmol) dropwise over 45 min. The red solution was stirred at −55 to −60 °C for 2.5 h. The reaction was then warmed to 0 °C in an ice bath. When the N_2 evolution stopped, approximately 20 min after it started, the solution was carefully quenched by the dropwise addition of 30 mL of D_2O (99.8% deuterium). The solution was then diluted with 500 mL of H_2O and 700 mL of pentane, while allowing for any 2-methylpropane present to boil off. The aqueous layer was extracted once with 500 mL and twice with 200 mL of pentane. The combined organic phases were washed four time with 300 mL of water. The pentane solution was then mixed with 300 mL of water and cooled in an ice bath. To this cooled mixture was added concentrated HCl until any remaining TMEDA was neutralized, pH 2. The organic layer was then washed with 500 mL of water, followed by 300 mL of saturated $NaHCO_3$. The pentane solution was dried over $MgSO_4$. After the solution was filtered, the pentane was removed by distillation through a 35-cm Vigreux column. The product was distilled through a 15-cm Vigreux column, and the fraction that distilled at 122–125 °C was collected. GC using the same conditions for the unlabeled diene (see above) also showed one major peak with a retention time of 3.1 min. A total of 11.72 g of material, 88% pure (GC), was collected in a yield of 70.7%. The product was typically 84–87% deuteriated, as shown by ^{1}H NMR: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.90 (s, 0.26 H), 5.71 (t, *J* = 2.3 Hz, 2 H), 3.03 (bs, 2 H), 2.07 (bs, 4 H); ^{2}H{^{1}H} NMR ($CHCl_3$, 46 MHz) δ 5.92 (s), 3.02 (trace); ^{13}C{^{1}H} NMR ($CDCl_3$, 22.5 MHz) δ 137.0 (t), 125.6, 40.3, 26.4; IR (neat, cm^{-1}) 3050 (s), 2920 (s), 2850 (s), 2320 (m), 2270 (m), 1645 (m), 1430 (m), 1258 (m), 1172 (m), 1045 (m), 1000 (m), 908 (m), 875 (m), 855 (m).

***trans*-3,4-Dibromobicyclo[4.2.0]oct-7-ene.** A suspension of freshly recrystallized pyridinium bromide perbromide (7.60 g, 23.8 mmol) in 50 mL of CH_2Cl_2 was prepared at −78 °C. To this suspension was added a solution of bicyclo[4.2.0]octa-3,7-diene (2.01 g, 19.0 mmol) in 15 mL of CH_2Cl_2 at once. The resulting solution was stirred at −78 °C for 6 h. After being warmed to room temperature, the solution was washed with 40 mL of water, 40 mL of saturated $Na_2S_2O_3$, and 40 mL of $NaHCO_3$. The organic phase was dried over $MgSO_4$. After filtration and removal of the solvent, the product was purified by two short-path distillations at 0.1 mmHg. The fraction from 67 to 72 °C was collected. A clear liquid product, *trans*-3,4-dibromobicyclo[4.2.0]oct-7-ene (4.41 g, 16.6 mmol), was isolated in a yield of 87.6%.

The material that remained in the distillation flask was flash chromatographed over a 4 cm by 25 cm silica column using 10% ethyl acetate in hexane, and a white solid (233 mg, 0.55 mmol), with an R_f of 0.48, was isolated. This minor product, which was *trans,trans*-3,4,7,8-tetrabromobicyclo[4.2.0]octane, was isolated in a 3% yield.

***trans*-3,4-Dibromobicyclo[4.2.0]oct-7-ene**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.25 (d, *J* = 2.8 Hz, 1 H), 6.07 (d, *J* = 2.8 Hz, 1 H), 4.68 (ddd, *J* = 7.1, 4.8, 4.8 Hz, 1 H), 4.45 (ddd, *J* = 7.1, 5.7, 5.7 Hz, 1 H), 3.14 (ddd, *J* = 4.4, 6.5, 5.8 Hz, 1 H), 3.00 (ddd, *J* = 4.4, 6.0, 6.5 Hz, 1 H), 2.53 (ddd, *J* = 15, 6.1, 6.1 Hz, 1 H), 2.30 (ddd, 1 H), 2.23 (ddd, 1 H), 2.11 (ddd, *J* = 15.0, 7.0, 7.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 140.8 (d), 138.6 (d), 54.6 (d), 54.1 (d), 39.3 (d), 39.0 (d), 36.1 (t), 35.0 (t); IR (neat, cm^{-1}) 3050 (m), 2940 (s), 1460 (m), 1430 (m), 1315 (m), 1290 (m), 1158 (m), 927 (m), 732 (s). Anal. Calcd for $C_8H_{10}Br_2$: C, 36.13; H, 3.79; Br, 60.08. Found: C, 36.09; H, 3.79; Br, 59.40.

***trans,trans*-3,4,7,8-Tetrabromobicyclo[4.2.0]octane.** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.07 (dd, *J* = 8.6, 8.6 Hz, 1 H), 4.67 (m, 1 H), 4.60 (m, 1 H), 4.51 (dd, *J* = 8.1, 8.1 Hz, 1 H), 3.04 (m, 1 H), 2.78 (ddd, *J* = 2.6, 10.8, 15.6 Hz, 1 H), 2.63 (m, 2 H), 2.20 (dm, *J* = 15.7 Hz, 1 H), 2.07 (ddd, *J* = 3.5, 7.7, 15.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 50.5 (d), 50.1 (d), 49.7 (d), 47.6 (d), 39.2 (d), 34.6 (d), 26.6 (t), 26.0 (t).

***exo*-9,10-Diaza-*trans*-4,5-dibromotricyclo[6.3.0.0^{2,7}]undeca-9-ene.** An ether solution of diazomethane was prepared by adding *N*-methyl-*N*-nitrosourea (0.0 g, 190 mmol) to a mixture of 50 mL of diethyl ether and 50 mL of 50% aqueous potassium hydroxide at 0 °C. After the two layers were allowed to separate, the organic layer was carefully decanted into a 125-mL flask. The ether solution was decanted a second time from any remaining water into a 50-mL round-bottomed flask, equipped with an O-ring joint, containing *trans*-3,4-dibromobicyclo[4.2.0]oct-7-ene (2.80 g, 10.5 mmol). The resulting solution was kept at room temperature under argon in the dark with occasional stirring for 18 days. Any remaining diazomethane was carefully quenched by adding a minimal amount of acetic acid. The ether was removed, and the product was purified by flash chromatography over a 6 cm × 16 cm silica column using 1:1 hexane/ethyl acetate. The fractions containing the product (R_f 0.31, in 1:1 hexane/ethyl acetate) were combined, and the product (3.19 g, 10.3 mmol) was isolated in a yield of 98%. The product apparently contained only two of the four possible stereoisomers: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.35 (bm, 0.5 H), 4.83 (bm, 0.5 H), 4.38–4.7 (m, 3.5 H), 4.30 (ddd, *J* = 2.2, 7.4, 17.8 Hz, 0.5 H), 2.98 (ddd, *J* = 6.7, 6.7, 6.7 Hz, 0.5 H), 2.73 (m, 1.5 H), 2.34 (m, 2.0 H), 2.40–2.63 (m, 1.5 H), 2.09 (dddd, *J* = 3.3, 8.1, 8.1, 8.1 Hz, 0.5 H), 1.98 (ddd, *J* = 4.0, 4.0, 17.6 Hz, 0.5 H), 1.82 (m, 0.5 H); ^{13}C NMR (benzene-d_6, 22.5 MHz) δ 92.1 (d), 91.2 (d), 82.9 (t), 82.6 (t), 51.7 (d), 50.9 (d), 50.5 (d), 50.0 (d), 36.4, 34.8, 34.4, 34.0, 33.3, 33.2, 33.1, 32.9, 30.7, 30.4; MS (CI − CH_4) *m/z* (relative intensity) 312 (3.0), 311 (28.2), 310 (7.1), 309 (58.4), 308 (4.0), 307 (30.2), 229 (6.4), 227 (5.7), 201 (5.0), 199 (5.7), 561 (3.0), 560 (3.0), 149 (25.5), 121 (7.1), 120 (28.5), 119 (100.0), 93 (18.3), 92 (4.0), 91 (26.5), 86 (10.5), 85 (4.0), 84 (17.3).

***trans*-4,5-Dibromo-*exo*-tricyclo[6.1.0.0^{2,7}]nonane.** A solution of *exo*-9,10-diaza-*trans*-4,5-dibromotricyclo[6.3.0.0^{2,7}]undeca-9-ene, (293.0 mg, 0.946 mmol) was prepared in 90 mL of dry benzene in a base-washed and oven-dried Pyrex 90-mL photoreactor that was purged with argon for 30 min. The solution was pumped to reflux and backfilled with argon three times. The solution was photolyzed for 8 h at room temperature with a medium-pressure Hg lamp. The solution was filtered through a plug of silica to remove any polymeric material. After the solvent was removed, the products were separated by flash chromatography over a 3 cm by 25 cm silica column using 0.8% ethyl acetate in hexane. The first fraction isolated (R_f 0.45, 2% ethyl acetate in hexane) (140.4 mg) was a mixture of two compounds. Analytical GC on a methylsilicone capillary column at 140 °C showed a ratio of 1.5:1 for two compounds having retention times of 5.89 and 3.70 min, respectively. The major compound was *trans*-4,5-dibromo-*exo*-tricyclo[6.1.0.0^{2,7}]nonane in a yield of 31.6%. The minor compound was one of two stereoisomers of *trans*-4,5-dibromo-1-methylene-2-vinylcyclohexane in a yield of 21.4%. The other fraction from the chromatography (R_f 0.33, 2% ethyl acetate in hexane) contained the other stereoisomer of *trans*-4,5-dibromo-1-methylene-2-vinylcyclohexane (47.6 mg, 0.169 mmol), isolated in a yield of 17.9%.

***trans*-4,5-Dibromotricyclo[6.1.0.0^{2,7}]nonane**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.80 (ddd, *J* = 4.5, 4.5, 4.5 Hz, 1 H), 4.33 (ddd, *J* = 4.5, 5.6, 9.6 Hz, 1 H), 2.39 (ddd, *J* = 4.5, 8.2, 14.2 Hz, 1 H), 2.31 (ddd, *J* = 6.0, 6.0, 14.3 Hz, 1 H), 2.14 (ddd, *J* = 9.4, 9.4, 14.3 Hz, 1 H), 2.09 (ddd, *J* = 5.6, 5.6, 14.3 Hz, 1 H), 2.05 (md, *J* = 1.8 Hz, 1 H), 1.89 (dddd, *J* = 1.5, 5.9, 5.9, 9.3 Hz, 1 H), 1.61 (dddd, *J* = 1.4, 1.4, 4.6, 5.9 Hz, 1 H), 1.47 (dddd, *J* = 1.5, 1.5, 4.6, 5.9 Hz, 1 H), 0.78 (ddd, *J* = 4.6, 5.9, 5.9 Hz, 1 H), 0.71 (ddd, *J* = 1.4, 1.4, 4.6 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 55.3 (d), 53.6 (d), 35.3 (t), 34.6 (d), 33.5 (t), 31.8 (d), 18.2 (d), 17.6 (d), 16.3 (t); MS (CI − CH_4) *m/z* (relative intensity) 283 (0.7), 282 (0.3), 281 (1.5), 280 (0.3), 279 (0.9), 201 (22.3), 199 (23.1), 121 (3.1), 120 (12.0), 119 (100.0), 91 (19.6).

***trans*-4,5-Dibromo-1-methylene-2-vinylcyclohexane (isomer a):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.88 (ddd, J = 7, 11, 17.5 Hz, 1 H), 5.16 (d, J = 11 Hz, 1 H), 5.11 (d, J = 17.5 Hz, 1 H), 4.87 (bd, J = 1 Hz, 2 H), 4.66 (ddd, J = 4, 4, 4 Hz, 1 H), 4.59 (ddd, J = 4, 4, 4 Hz, 1 H), 3.28 (bd, J = 14.5 Hz, 1 H), 3.22 (m, 1 H), 2.58 (dd, J = 4, 15 Hz, 1 H), 2.45 (m, 1 H), 2.1 (m, 1 H).

***trans*-4,5-Dibromo-1-methylene-2-vinylcyclohexane (isomer b):** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.77 (ddd, J = 8, 11, 17.5 Hz, 1 H), 5.13 (d, J = 11 Hz, 1 H), 5.06 (d, J = 17.5 Hz, 1 H), 4.86 (d, J = 1.5 Hz, 1 H), 4.76 (d, J = 1.5 Hz, 1 H), 4.18 (ddd, J = 5, 12.5, 12.5 Hz, 1 H), 4.02 (ddd, J = 5, 11.5, 12.5 Hz, 1 H), 3.07 (dd, J = 5, 14.0 Hz, 1 H), 2.77 (m, 1 H), 2.63 (dm, J = 14.0 Hz, 1 H), 2.57 (ddd, J = 5, 5, 14.0 Hz, 1 H), 1.89 (ddd, J = 12.5, 12.5, 12.5 Hz, 1 H).

For preparative purposes, removal of the unwanted byproducts was most effectively achieved by oxidizing them with *m*-chloroperoxybenzoic acid (MCPBA) and then chromatographing the mixture. A typical procedure was as follows.

A solution of *exo*-9,10-diaza-*trans*-4,5-dibromotricyclo[6.3.0.0^{2,7}]undeca-9-ene (896.3 mg, 2.90 mmol) in benzene was photolyzed as above. After removal of the benzene the crude product mixture was treated with 85% MCPBA (244 mg, 1.4 mmol) in 6.0 mL of dichloromethane for 12 h at room temperature. The solution containing precipitated *m*-chlorobenzoic acid was washed with 5.0 mL of saturated $NaHCO_3$, 5.0 mL of saturated $Na_2S_2O_3$, and again with 5.0 mL of saturated $NaHCO_3$. After the solution was dried over $MgSO_4$ and the solvent was removed, the product was purified by flash chromatography over a 3 cm by 20 cm silica column using 0.8% ethyl acetate in hexane. The fractions containing product (R_f 0.45, 2% ethyl acetate in hexane), were combined to give pure *trans*-4,5-dibromotricyclo[6.1.0.0^{2,7}]nonane (264.4 mg, 0.9392 mmol) in a yield of 32.5%.

Bicyclo[6.1.0]nona-2,4,6-triene. A reference sample of bicyclo[6.1.0]nona-2,4,6-triene was prepared by the method of Katz and Garratt.[23]

A suspension of anhydrous lithium carbonate (3.88 g, 52.5 mmol) and anhydrous lithium bromide (4.56 g, 52.5 mmol) in 90 mL of freshly distilled HMPA was prepared in a dry 250-mL round-bottomed equipped with a mechanical stirrer. To this suspension was added *trans*-4,5-dibromotricyclo[6.1.0.0^{2,7}]nonane (1.48 g, 5.25 mmol) at once with a syringe. The stirring suspension was then immersed in a preheated 60–62 °C oil bath for 4 h. The solution was cooled to room temperature over an hour. The suspension was diluted with 150 mL of water and then extracted with two 200-mL and two 100-mL portions of pentane. The combined organic extracts were then washed five times with 100 mL of water, once with 100 mL of 0.5 M HCl, and once with 100 mL of saturated $NaHCO_3$. After the solution was dried over $MgSO_4$ and the solvent was removed, the product was purified by vacuum transfer. A clear liquid product, bicyclo[6.1.0]nona-2,4,6-triene (529 mg, 4.41 mmol), was isolated in a yield of 85%. The product typically contained small amounts of dihydroindene: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.98 (m, 6 H), 1.40 (dd, J = 6.2, 9.2 Hz, 2 H), 1.00 (td, J = 9.2, 3.5 Hz, 1 H), 0.04 (td, J = 6.2, 3.5 Hz, 1 H); ^{13}C NMR (benzene-d_6, 22.5 MHz) δ 130.0 (d), 128.1 (d), 125.5 (d), 17.2 (d), 14.1 (t); MS (EI) m/z (relative intensity) 120 (0.2), 119 (5.5), 118 (M^+, 59.9), 117 (100.0), 116 (10.1), 115 (30.0), 92 (3.3), 91 (30.0); MS (CI – CH_4) m/z (relative intensity) 121 (1.1), 120 (11.8), 119 (100.0), 118 (28.1), 117 (79.4), 92 (6.8), 91 (79.9).

***trans*-3,4-Dibromobicyclo[4.2.0]oct-7-ene-*7,8-d*$_2$.** A solution of bicyclo[4.2.0]octa-3,7-diene-*7,8-d*$_2$ (11.62 g, 95.5 mmol) in 165 mL of dry chloroform was cooled to −55 to −60 °C. To this cooled solution was 80+% pyridinium bromide perbromide, (39.41 g, 98.7 mmol) at once. After the solution was stirred for 1.5 h, the orange color faded and the solution was warmed to room temperature. The solution was diluted with 50 mL of dichloromethane and washed with 50 mL of saturated $Na_2S_2O_3$ and with 50 mL of saturated $NaHCO_3$. The solution was dried over $MgSO_4$, and the solvent was removed. The product was distilled at 0.1 mmHg, and the fraction that distilled from 72 to 80 °C was collected. A clear liquid product, *trans*-3,4-dibromobicyclo[4.2.0]oct-7-ene-*7,8-d*$_2$ (23.98 g, 89.49 mmol), was isolated in a yield of 93.7%: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.25 (s, 0.13 H, 6.07 (s, 0.13 H), 4.68 (ddd, J = 4.8, 4.8, 7.1 Hz, 1 H), 4.45 (ddd, J = 5.7, 5.7, 7.1 Hz, 1 H), 3.14 (ddd, J = 4.4, 5.8, 6.5 Hz, 1 H), 3.00 (ddd, J = 4.4, 6.0, 6.5 Hz, 1 H), 2.53 (ddd, J = 6.1, 6.1, 15.0 Hz, 1 H), 2.30 (ddd, 1 H), 2.23 (ddd, 1 H), 2.11 (ddd, J = 7.0, 7.0, 15.0 Hz, 1 H); ^{2}H{^{1}H} NMR ($CHCl_3$, 46 MHz) δ 6.28 (s, 1 D), 6.10 (s, 1 D); ^{13}C{^{1}H} NMR ($CDCl_3$, 22.5 MHz) δ 140.4 (t), 138.8 (t), 54.8, 54.2, 39.3, 39.0, 36.2, 35.2; IR (neat, cm^{-1}) 2910 (s), 2270 (w), 1460 (m), 1425 (m), 1155 (m), 922 (m).

***exo*-9,10-Diaza-*trans*-4,5-dibromotricyclo[6.3.0.0^{2,7}]undeca-9-ene-*1,8-d*$_2$.** A solution of *trans*-3,4-dibromobicyclo[4.2.0]oct-7-ene-*7,8-d*$_2$ (8.03 g, 29.99 mmol) in 100 mL of diethyl ether containing diazomethane from *N*-methyl-*N*-nitrosourea (40.00 g, 380 mmol) was prepared as in the procedure for the synthesis of the unlabeled material. The solution was kept under N_2, at room temperature, in the dark, with occasional stirring for 21 days. The unreacted diazomethane was quenched by the addition of a minimal amount of acetic acid. The solvent was removed, and the product was purified by flash chromatography over a 7.5 cm by 18 cm silica column using 1:1 hexane/ethyl acetate. The fractions containing product (R_f 0.33, 1:1 hexane/ethyl acetate) were combined to give the desired adduct (9.28 g, 29.95 mmol) in a yield of 99.9%: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.35 (trace), 4.83 (trace), 4.38–4.70 (m, 3.5 H), 4.30 (bd, J = 17.6 Hz, 0.5 H), 2.98 (trace), 2.65–2.82 (m, 1.5 H), 2.55 (ddd, J = 5.2, 7.6, 16.0 Hz, 0.5 H), 2.40–2.52 (m, 1 H), 2.32 (m, 1.5 H), 2.09 (ddd, J = 8.0, 8.0, 8.0 Hz, 0.5 H), 1.99 (ddd, J = 4.2, 4.2, 16.2 Hz, 0.5 H), 1.87 (ddd, J = 3.8, 7.6, 7.6 Hz, 0.5 H); ^{2}H{^{1}H} NMR ($CHCl_3$, 46 MHz) δ 5.23 (0.5 D), 4.83 (0.5 D), 2.90 (0.5 D), 2.25 (0.5 D); ^{13}C{^{1}H} NMR ($CDCl_3$, 22.5 MHz) δ 90.8 (t), 90.1 (t), 82.4, 82.0, 51.8, 51.0, 50.8, 50.0, 35.8, 34.0, 33.8, 33.2, 32.9, 32.8, 32.7, 32.6, 30.4, 30.1; IR (thin film, cm^{-1}) 2930 (m), 2190 (w), 1420 (m), 1165 (m); MS (CI – isobutane) m/z (relative intensity) 314 (4.20), 313 (28.77), 312 (19.27), 311 (60.07), 310 (25.27), 309 (30.45), 308 (10.74), 122 (5.23), 121 (18.53), 120 (7.74).

***trans*-4,5-Dibromotricyclo[6.1.0.0^{2,7}]nonane-*1,8-d*$_2$.** A base-washed, oven-dried, 500-mL Pyrex photoreactor was flushed with argon for 30 min and chaarged with *exo*-9,10-diaza-*trans*-4,5-dibromotricyclo[6.3.0.0^{2,7}]undeca-9-ene-*1,8-d*$_2$ (6.00 g, 19.3 mmol). Approximately 500 mL of dry and oxygen-free benzene was then transferred to the photoreactor with a cannula. The solution was photolyzed with a medium-pressure Hg lamp for 12 h at room temperature. The solution was passed through a plug of silica to remove any polymeric material. The benzene was removed, and the products were purified by flash chromatography over a 4 cm by 15 cm silica column using 0.8% ethyl acetate in hexane. A minor fraction (R_f 0.48, 2% ethyl acetate in hexane), which contained *trans*-4,5-dibromo-1-(methylene-*d*)-2-(vinyl-*1-d*)cyclohexane (isomer b), was collected.

The major fraction (R_f 0.38, 2% ethyl acetate in hexane) (3.64 g) was treated with 80% MCPBA (2.00 g, 9.3 mmol) in 60 mL of dichloromethane at room temperature for 12 h. The solution was diluted with 50 mL of dichloromethane and washed once with 25 mL of saturated $Na_2S_2O_3$ and twice with 25 mL of saturated $NaHCO_3$. The solution was dried over $MgSO_4$, and the solvent was removed. The product was purified by flash chromatography over 4 cm by 16 cm silica column using 0.8% ethyl acetate in hexane. The fractions containing product (R_f 0.38, 2% ethyl acetate in hexane) were combined, and *trans*-4,5-dibromotricyclo[6.1.0.0^{2,7}]nonane-*1,8-d*$_2$ (1.72 g, 6.11 mmol) was obtained in a yield of 31.6%: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.80 (ddd, J = 4.5, 4.5, 4.5 Hz, 1 H), 4.33 (ddd, J = 4.5, 5.6, 9.6 Hz, 1 H), 2.39 (ddd, J = 4.4, 8.3, 14.1 Hz, 1 H), 2.31 (ddd, J = 6.0, 6.0, 14.3 Hz, 1 H), 2.14 (ddd, J = 9.5, 9.5, 14.3 Hz, 1 H), 2.09 (ddd, J = 5.6, 5.6, 14.3 Hz, 1 H), 2.03 (ddd, J = 5.7, 5.7, 8,9 Hz, 1 H), 1.89 (ddd, J = 5.9, 5.9, 9.2 Hz, 1 H), 1.61 (trace), 1.47 (trace), 0.78 (d, J = 4.6 Hz, 1 H), 0.71 (d, J = 4.6 Hz, 1 H); ^{2}H{^{1}H} NMR ($CHCl_3$, 46 MHz) δ 1.61 (1 D), 1.47 (1 D), 2.04 (0.02 D), 1.85 (0.02 D); ^{13}C{^{1}H} NMR ($CDCl_3$, 22.5 MHz) δ 55.2, 53.6, 35.2, 34.3, 33.4, 31.6, 17.6 (t), 17.0 (t), 16.0; IR (neat, cm^{-1}) 3050 (m), 2920 (s), 2200 (m), 1460 (m), 1424 (m), 1163 (m), 995 (m).

Bicyclo[6.1.0]nona-2,4,6-triene-*1,8-d*$_2$ (1-*d*$_2$). An oven-dried, three-neck 500-mL round-bottomed flask equipped with a mechanical stirrer was charged with lithium carbonate (7.87 g, 107 mmol), lithium bromide, (9.24 g, 107 mmol), and 180 mL of freshly distilled HMPA. The suspension was heated in an oil bath

(23) Katz, T. J.; Garratt, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 5194.

regulated by a Precision Scientific relay, at 64–65 °C. To this warmed suspension was added *trans*-4,5-dibromotricyclo-[6.1.0.0^{2,7}]nonane-*1,8-d*$_2$ (3.00 g, 10.65 mmol). The solution was heated for 4.25 h. After being cooled to room temperature, the reaction was treated in the same manner as described for the synthesis of the unlabeled material. A clear liquid material (1.14 g) was isolated. Analytical GC on a methylsilicone capillary column at 60 °C and in injector temperature of 85 °C showed that this material was 89% product (retention time of 6.6 min) for a yield of 79%: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.98 (m, 6 H), 1.40 (0.26 H), 1.00 (bd, J = 3.5 Hz, 1 H), 0.04 (bd, J = 3.5 Hz, 1 H); ^{2}H{^{1}H} NMR ($CHCl_3$, 46 MHz) δ 5.96 (0.04 D), 1.42 (2.0 D); ^{13}C{^{1}H} NMR ($CDCl_3$, 22.5 MHz) δ 129.9, 127.6, 125.1, 15.7 (t), 13.5; IR (neat, cm^{-1}) 3020 (s), 2880 (m), 2230 (m), 1648 (m), 1630 (m), 1080 (m), 882 (m).

***endo*-9-Bromobicyclo[6.1.0]nona-2,4,6-triene.** Potassium cyclooctatetraenide was prepared as described by Katz and Garratt for the preparation of *exo*-9-chlorobicyclo[6.1.0]nona-2,4,6-triene.[24] A suspension of potassium metal (30.0 g, 767 mmol), cut in small pieces, in 500 mL of dry THF was prepared and cooled to −78 °C. To this suspension was added freshly distilled cyclooctatetraene (34.00 g, 380 mmol) at once with a syringe. The solution was stirred at −78 °C for 4 h. The solution was warmed to room temperature and stirred overnight.

A second solution of 150 mL of freshly distilled bromoform and 250 mL of THF was prepared in a 1000-mL round-bottomed flask equipped with a pressure equalizing addition funnel and a mechanical stirrer. The potassium cyclooctatetraenide solution was transferred via cannula to the addition funnel. Any of the dianion that had precipitated out of solution was taken up in an additional 100 mL of THF. The bromoform solution was cooled to −78 °C, and the potassium cyclooctatetraenide solution was added dropwise over 6 h. The solution was warmed to room temperature over 4 h. After any unreacted dianion was quenched by the slow addition of 50 mL of absolute ethanol, the solution was washed three times with 200 mL of water and dried over $MgSO_4$ and the THF removed. The residue was distilled at 0.1 mmHg. Any remaining bromoform was distilled below 30 °C, and the fraction that distilled from 35 to 70 °C was collected. This fraction, which is a mixture of desired product and bromodihydroindene, was purified by flash chromatography over silica using 0.5% ethyl acetate in hexane. When the mixture was added to the column, a mild exothermic reaction took place, probably the conversion of the bromodihydroindene to indene. The fractions containing the product (R_f 0.34 in 2% ethyl acetate in hexane) were combined (13.46 g, 68.4 mmol) for a yield of 18.0%: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 5.86 (m, 6 H), 3.41 (t, J = 7.5 Hz, 1 H), 1.87 (d, J = 7.5 Hz, 2 H); ^{13}C{^{1}H} (benzene-d_6, 22.5 MHz), δ 130.7, 127.1, 126.2, 29.2, 20.7.

Bicyclo[6.1.0]nona-2,4,6-triene-*endo*-9-*d* (1-*endo*-9-*d*). Bicyclo[6.1.0]nona-2,4,6-triene-*endo*-9-*d* was synthesized by the procedure of Lewis and Brookhart.[25] The product was stored at −78 °C.

***endo*-9-Chlorobicyclo[6.1.0]nona-2,4,6-triene.** A solution of *endo*-9-bromobicyclo[6.1.0]nona-2,4,6-triene (1.00 g, 5.08 mmol) in 25 mL of THF was prepared and cooled to −78 °C. To this solution was added a 1.32 M *n*-butyllithium in hexane (3.85 mL, 5.08 mmol) in 3 min. The solution quickly turned a green color. After being stirred for 15 min, a solution of recrystallized hexachloroethane (2.47 g, 10.40 mmol) in 25 mL of THF was added dropwise over 5 min. The solution was slowly warmed to −50 °C and stirred for 25 min before being warmed to room temperature. The solution was mixed with 50 mL of water and extracted with two 50 mL portions of hexane. The organic solution was dried over $MgSO_4$, and the solvent was removed. The product was purified by flash chromatography over a 5 cm by 35 cm silica column using 0.5% ethyl acetate in hexane. Fractions containing product (R_f 0.24 in 2% ethyl acetate in hexane) were combined. The solvent was removed, and the product was further purified by vacuum transfer to give *endo*-9-chlorobicyclo[6.1.0]nona-2,4,6-triene (360 mg, 2.36 mmol) in a yield of 46.5%: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.12 (d, J = 12.4 Hz, 2 H), 5.86 (s, 2 H), 5.83 (d, J = 12.4 Hz, 2 H), 3.46 (t, J = 7.4 Hz, 1 H), 1.82 (d, J = 7.4 Hz, 2 H); ^{13}C{^{1}H} NMR (benzene-d_6, 22.5 MHz) δ 131.1, 126.2, 125.6, 37.3, 20.8.

9,9-Dibromobicyclo[6.1.0]nona-2,4,6-triene. 9,9-Dibromobicyclo[6.1.0]nona-2,4,6-triene was prepared by the procedure of Boche, Weber, Martens, and Bieberbach with the modification that a vibromixer was used in place of a stirrer:[26] ^{1}H NMR ($CDCl_3$, 80 MHz) δ 5.90 (m, 6 H), 2.45 (s, 2 H); ^{13}C NMR (benzene-d_6, 22.5 MHz) δ 130.2 (d), 126.0 (d), 125.6 (d), 34.8 (d and s).

***exo*-9-Bromobicyclo[6.1.0]nona-2,4,6-triene.** *exo*-9-Bromobicyclo[6.1.0]nona-2,4,6-triene was prepared by a modified version of a procedure in the literature.[23]

A solution of 9,9-dibromobicyclo[6.1.0]nona-2,4,6-triene (6.00 g, 21.8 mmol) was prepared in 80 mL of THF and cooled in a −97 °C methanol slush bath. To this solution 1.1 M *n*-butyllithium in hexane (24 mL, 26.4 mmol) was added over 5 min. The green solution was stirred for 10 min at −97 °C before it was quenched by the slow addition of 10 mL of methanol. The red solution was warmed to room temperature and washed with 200 mL of water. The water was washed with three 100-mL portions of hexane. After the solution was dried over $MgSO_4$ and the solvent was removed, the product was purified by flash chromatography over 5 cm × 35 cm silica column using 0.5% ethyl acetate in hexane. Two fractions (R_f 0.46 and 0.37 in 2% ethyl acetate in hexane) were isolated. The first fraction contained *exo*-9-bromobicyclo-[6.1.0]nona-2,4,6-triene (2.35 g, 11.93 mmol) in a yield of 54.9%. The second fraction contained *endo*-9-bromobicyclo[6.1.0]nona-2,4,6-triene (450 mg, 2.29 mmol) in a yield of 10.5%: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 6.01 (s, 4 H), 5.88 (s, 2 H), 2.42 (t, J = 4.3 Hz, 1 H), 1.92 (d, J = 4.3 Hz, 2 H); ^{13}C NMR (benzene-d_6, 22.5 MHz) δ 128.6 (d), 125.8 (d), 125.2 (d), 28.7 (d), 25.2 (d).

Bicyclo[6.1.0]nona-2,4,6-triene-*exo*-9-*d* (1-*exo*-9-*d*). A solution of *exo*-9-bromobicyclo[6.1.0]nona-2,4,6-triene (1.30 g, 6.60 mmol) in 25 mL of THF at −60 °C was treated with 2.0 M *tert*-butyllithium in pentane (6.6 mL, 13.2 mmol) over 4 min. The resulting green solution was stirred at −60 °C for 5.5 min. The solution was cooled to −78 °C and quenched with 4 mL of methanol-*d*. The cold solution was diluted with 40 mL of −20 °C isopentane. The cold solution was washed with 80 mL of cold water. The water was then extracted with three 25-mL portions of cold isopentane.. The combined organic layers were washed with two 25-mL portions of saturated NaCl. The solution was dried at −78 °C over $MgSO_4$. The solution was filtered, and the isopentane and THF were removed under vacuum at −78 to −55 °C. The product was vacuum transferred at 0 °C to give a solution (1.4 g) of 48% product (GC) in a mixture of isopentane and THF. The solution also contained a trace of indene. The desired compound was obtained in a yield of 86%. The solution containing bicyclo[6.1.0]nona-2,4,6-triene-*exo*-9-*d* could be stored at −78 °C for a few days without epimerization.

***exo*-9-Chlorobicyclo[6.1.0]nona-2,4,6-triene.** A modified version of the literature procedure was used.[20]

Potassium cyclooctatetraenide was prepared by adding cyclooctatetraene (26.6 g, 0.256 mmol) to a suspension of potassium metal (20.0 g, 592 mmol) in 400 mL of the THF and cooled to −78 °C. After being stirred for 3 h at −78 °C, the solution was warmed to room temperature and stirred for ten hours.

A second solution containing 250 mL of chloroform and 100 mL of THF was prepared in 1000-mL round-bottomed flask equipped with a pressure equalizing addition funnel and a mechanical stirrer. The potassium cyclooctatraenide solution, which was transferred to the addition funnel via a cannula, was added dropwise to the chloroform solution at −78 °C over 3 h. The solution was warmed to room temperature and stirred for 3 h, and then any remaining dianion was quenched by the slow addition of 30 mL of absolute ethanol. The solution was diluted with 500 mL of water. The aqueous layer was extracted with two 125-mL portions of diethyl ether. The combined organic solutions were washed three times with 100 mL of saturated NaCl and dried over $MgSO_4$. The solvent was removed, and the product was distilled through a 14-cm Vigreux column at 0.2 mmHg. The fraction that distilled from 35 to 42 °C (4.50 g) was of a mixture

(24) Katz, T. J.; Garratt, P. J. *J. Am. Chem. Soc.* **1964**, *86*, 4876.
(25) (a) Lewis, C. P.; Brookhart, M. *J. Am. Chem. Soc.* **1975**, *97*, 651. (b) Lewis, C. P. Ph.D. dissertation, University of North Carolina, Chapel Hill, 1976, p 79.
(26) Boche, G.; Weber, H.; Martens, D.; Biecherbach, A. *Chem. Ber.* **1978**, *111*, 2480.

of the product and cyclooctatetraene. The fraction that distilled from 42 to 45 °C was a 10:1 (NMR) mixture of *exo*- and *endo*-9-chlorobicyclo[6.1.0]nona-2,4,6-triene. This fraction (19.50 g, 128 mmol) was collected in a yield of 50%.

The desired product could be separated from its epimer by flash chromatography over silica using 0.5% ethyl acetate in hexane: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.00 (s, 4 H), 5.87 (s, 2 H), 2.52 (t, J = 4.1 Hz, 1 H), 2.52 (d, J = 4.1 Hz, 2 H); ^{13}C{^{1}H} NMR (benzene-d_6, 22.5 MHz) δ 128.9, 125.7, 125.1, 38.7, 28.7.

(Diglyme)tricarbonylmolybdenum. The procedure was based on the work of Werner and Coffield.[27]

A 250-mL single-neck round-bottomed flask was charged with sublimed molybdenum hexacarbonyl (37.5 g, 142 mmol), 38 mL of freshly distilled benzene, and 125 mL of freshly distilled diglyme. The flask was equipped with a 11-cm reflux tube connected to a size C filter frit. The solution was cooled to −78 °C and pumped to vacuum and backfilled with argon four times. The solution was then refluxed under an atmosphere of argon in a 128–132 °C oil bath for 36 h. The temperature of the bath was maintained with a Precision Scientific relay. The yellow solution was filtered while hot, and the filtrate was cooled to −78 °C. The cold solution was back-filtered leaving a mixture of product and molybdenum hexacarbonyl. The flask containing the filtrate was removed under a flow of argon and replaced with a 5-mL flask. The solid was dried overnight under vacuum. The unreacted molybdenum hexacarbonyl was removed by sublimation at 60 °C and 0.001 mmHg. A yellow, very air-sensitive solid (13.0 g, 41.4 mmol) was obtained in a yield of 29.2%.

(Bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum. (Bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum was prepared by a procedure similar to that of Grimme.[1] A two-neck 50-mL round-bottomed flask was charged with (diglyme) tricarbonylmolybdenum, (1.70 g, 5.41 mmol). The flask, a straight gas line adapter, and a size D filter frit were assembled in a drybox. To this was added 5 mL of THF by vacuum transfer. To the resulting suspension at −78 °C was added bicyclo[6.1.0]nona-2,4,6-triene (970 mg, 8.22 mmol) with a syringe through the gas line adapter under a flow of argon. The solution was pumped to reflux and backfilled with argon three times. The solution was warmed to room temperature and stirred for 4 h. The THF was removed and 45 mL of hexane was added by vacuum transfer. The product was extracted in the refluxing hexane. The hexane was filtered while hot, concentrated to 20 mL, and slowly cooled to −78 °C. The solution was filtered, leaving the orange product, which was dried under vacuum. The orange solid was sublimed at 0.01 mmHg and 90 °C to give (bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum (1.28 g, 4.30 mmol) in a yield of 79.5%: ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 5.91 (dd, J = 5.0, 2.5 Hz, 2 H), 5.36 (ddd, 2 H), 4.86 (bd, 2 H), 1.04 (bdd, J = 5.0, 8.6 Hz, 2 H), 0.75 (td, 1 H), 0.30 (td, 1 H); ^{1}H NMR (C_6D_{12}, 300 MHz) δ 5.71 (dd, J = 5.0, 2.5 Hz, 2 H), 5.17 (ddd, 2 H), 4.61 (bd, 2 H), 0.91 (ddd, J = 0.70, 5.0, 8.6 Hz, 2 H), 0.64 (td, 1 H), 0.36 (td, 1 H); ^{1}H NMR (benzene-d_6, 300 MHz) δ 5.01 (dd, 2 H), 4.72 (ddd, 2 H), 4.36 (d, 2 H), 0.55 (dd, 2 H), 0.35 (td, 1 H), 0.27 (td, 1 H); ^{13}C{^{1}H} NMR (benzene-d_6, 22.5 MHz) δ 101.4, 97.0, 88.5, 19.2, 12.6.

(Bicyclo[6.1.0]nona-2,4,6-triene-*1,8-d*$_2$)tricarbonylmolybdenum. The procedure for the synthesis of the unlabeled complex was followed, using (diglyme)tricarbonylmolybdenum (2.00 g, 6.36 mmol) and bicyclo[6.1.0]nona-2,4,6-triene-*1,8-d*$_2$ (1.04 g, 7.45 mmol) (86% pure). The product was pure after one recrystallization and so was not sublimed. It was obtained in a yield of 80.8%: ^{1}H NMR (benzene-d_6, 300 MHz) δ 5.01 (dd, 1.99 ± 0.02 H), 4.72 (ddd, 2.02 ± 0.01 H), 4.36 (d, 1.99 ± 0.02 H), 0.55 (0.267 ± 0.007 H), 0.35 (d, 1.00 ± 0.01 H), 0.27 (d, 1.01 ± 0.01); ^{2}H{^{1}H} NMR (benzene, 46 MHz) δ 4.41 (0.040 ± 0.002 H), 0.58 (2.00 ± 0.01 H).

(Bicyclo[6.1.0]nona-2,4,6-triene-*endo*-9-*d*)tricarbonylmolybdenum. A procedure similar to that of Lewis[25b] was used. A two-neck 50-mL round-bottomed flask containing (diglyme)-tricarbonylmolybdenum (2.90 g, 9.22 mmol) was equipped in a drybox with a straight gas line adaptor and a size D filter frit. A suspension of the (diglyme)tricarbonylmolybdenum in 10 mL of THF was prepared at −78 °C. To this suspension was added a cold 80% (GC) solution of 1-*endo*-9-*d* (1.6 mL, 9.1 mmol) in THF. The solution was pumped to reflux and backfilled with argon three times. The solution was warmed to 0 °C and stirred in an ice bath for 3 h. The THF and unreacted 1-*endo*-9-*d* were removed under vacuum, and the product was taken-up in 40 mL of 60 °C hexane. The hot hexane solution was filtered and concentrated to 25 mL. The solution was slowly cooled to −78 °C and filtered. After the solution was dried under vacujm, the orange product was sublimed at 90 °C and 0.01 mmHg to give the product (1.80 g, 6.02 mmol) in a yield of 66.2%. The preparation was carried out twice with different endo and exo deuterium ratios.

Batch 1: ^{2}H{^{1}H} NMR (CH_2Cl_2, 46 MHz) δ 0.77 (0.066 ± 0.002 D), 0.33 (0.93 ± 0.01 D).

Batch 2: ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 5.95 (dd, 2.00 ± 0.01 H), 5.36 (ddd + $CDHCl_2$) 4.86 (dd, 2.00 ± 0.02 H), 1.04 (d, 2.00 ± 0.02 H), 0.75 (t, 1.00 ± 0.01 H), 0.30 (0.27 ± 0.02 H); ^{2}H{^{1}H} NMR (CH_2Cl_2, 46 MHz) δ 0.77 (0.0155 ± 0.0005 D), 0.33 (0.985 ± 0.004 D).

(Bicyclo[6.1.0]nona-2,4,6-triene-*exo*-9-*d*)tricarbonylmolybdenum, prepared by the same procedure used for the *endo*-9-*d* epimer: ^{1}H NMR (C_6D_{12}, 300 MHz) δ 5.71 (dd, 2.00 ± 0.03 H), 5.17 (ddd, 2.00 ± 0.01 H), 4.61 (d, 2.01 ± 0.02 H), 0.91 (m, 2.00 ± 0.02 H), 0.64 (0.47 ± 0.02 H), 0.36 (m, 0.96 ± 0.01 H).

(*exo*-9-Bromobicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum. A 25-mL two-neck round-bottomed flask equipped with a size D filter frit and a straight gas line adapter was charged with (diglyme)tricarbonylmolybdenum (700 mg, 2.23 mmol), in a drybox. To a suspension of (diglyme)tricarbonylmolybdenum in 5 mL of THF was added *exo*-9-bromobicyclo[6.1.0]nona-2,4,6-triene (540 mg, 2.74 mmol) at once with a syringe through the gas inlet adapter, under a flow of argon. The solution was pumped to reflux and backfilled with argon three times. The solution was warmed to 0 °C and stirred for 3 h. Once at 0 °C, the (diglyme)tricarbonylmolybdenum went into solution as it reacted and the solution slowly turned a reddish brown. The THF was removed, and the product was extracted with 23 mL of hexane at reflux. The solution was filtered while still hot and cooled to −78 °C. The cold solution was back-filtered into the reaction flask, and the material in the flask was extracted for a second time with refluxing hexane. The solution was filtered, reduced to 10 mL, and cooled to −78 °C. The precipitated product was filtered and dried under vacuum. The product was isolated as an orange solid (370 mg, 0.98 mmol) in a yield of 44.0%: ^{1}H NMR (benzene-d_6, 300 MHz) δ 4.87 (dd, J = 5.1, 2.5 Hz, 2 H), 4.49 (ddd, 2 H), 4.00 (bd, 2 H), 2.61 (t, J = 3.3 Hz, 1 H), 1.01 (bd, 2 H); ^{13}C{^{1}H} NMR (benzene-d_6, 22.5 MHz) δ 101.1, 95.9, 82.8, 30.8, 23.3; IR (solution—C_6H_{12}, cm^{-1}) 2003 ns), 1998 (s), 1931 (s).

(*exo*-9-Chlorobicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum. A 25-mL round-bottomed flask containing (diglyme)tricarbonylmolybdenum (360 mg, 1.1 mmol) was assembled with a size D filter frit and a straight gas line adapter, in a drybox. To a suspension of (diglyme)tricarbonylmolybdenum in 5 mL of THF at −78 °C was added *exo*-9-chlorobicyclo-[6.1.0]nona-2,4,6-triene (260 mg, 1.70 mmol) with a syringe through the gas line adapter, under a flow of argon. The solution was pumped to reflux and backfilled with argon three times. The solution was warmed to room temperature and stirred for 2.5 h, during which time it turned a reddish brown color. The THF was removed, and the resulting solid was extracted with 20 mL of 30 °C diethyl ether. The warm ether solution was filtered and concentrated to 5 mL. The ether solution was then diluted with 20 mL of hexane and heated to reflux. The solution was then slowly cooled to −78 °C and back-filtered, leaving an orange solid (210 mg, 0.63 mmol) in a yield of 57.4%: ^{1}H NMR (benzene-d_6, 300 MHz) δ 4.87 (dd, J = 5.0, 2.5 Hz, 2 H), 4.50 (ddd, 2 H), 4.00 (d, 2 H), 2.77 (t, J = 3.1 Hz, 1 H), 0.98 (d, 2 H); ^{13}C{^{1}H} NMR (benzene-d_6, 22.5 MHz) δ 101.1, 96.0, 82.5, 37.3, 30.6.

(*endo*-9-Chlorobicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum. (*endo*-9-Chlorobicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum was prepared from (diglyme)tricarbonylmolybdenum (350 mg, 1.1 mmol) and *endo*-9-chlorobicyclo[6.1.0]nona-2,4,6-triene (260 mg, 1.7 mmol) by using the same method that was used for the preparation of the exo epimer. An orange solid product (180 mg, 0.56 mmol) was isolated in a yield of 50.8%. The presence of two isomers, in a ratio of

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3:1, was indicated by the NMR data. The two isomers were not separated.

Major isomer: ^{1}H NMR (benzene-d_6, 300 MHz) δ 4.81 (m, 4 H), 4.12 (d, J = 10.4 Hz, 2 H), 2.50 (t, J = 7.5 Hz, 1 H), 0.59 (d, J = 7.5 Hz, 2 H); ^{13}C{^{1}H} NMR (benzene-d_6, 22.5 MHz) δ 100.2, 97.8, 82.0, 36.7, 26.1.

Minor isomer: ^{1}H NMR (benzene-d_6, 300 MHz) δ 5.35 (s, 2 H), 4.81 (m, 2 H), 3.79 (d, J = 9.5 Hz, 2 H), 3.07 (t, J = 5.2 Hz, 1 H), 0.99 (d, J = 5.2 Hz, 2 H); ^{13}C{^{1}H} NMR (benzene-d_6, 22.5 MHz) δ 131.2, 102.8, 98.6, 52.7, 18.1.

(9,9-Dibromobicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum. A 25-mL round-bottomed flask containing 9,9-dibromobicyclo[6.1.0]nona-2,4,6-triene (460 mg, 1.67 mmol) and (diglyme)tricarbonylmolybdenum (500 mg, 1.60 mmol) was assembled with a size D filter frit in a drybox. After 5 mL of THF was added by vacuum transfer, the solution was warmed to room temperature and stirred for 4 h. The THF was removed, and the remaining solid material was treated in the same manner as in the preparation of the exo 9-bromo complex. An orange-brown solid (190 mg, 0.42 mmol) was isolated in a yield of 26.3%.

The presence of two isomers in a ratio of 3.8:1 was indicated by the NMR data. The isomers were not separated.

Major isomer: ^{1}H NMR (benzene-d_6, 300 MHz) δ 5.22 (s, 2 H), 4.50 (d, J = 9.3 Hz, 1 H), 3.57 (d, J = 9.3 Hz, 2 H), 1.68 (s, 2 H); ^{13}C (benzene-d_6, 22.5 MHz) δ 131.5 (d), 98.6 (d), 96.7 (d), 44.2 (s), 31.3 (d).

Minor isomer: ^{1}H NMR (benzene-d_6, 300 MHz) δ 4.65 (m, 4 H), 3.92 (d, J = 9.6 Hz, 2 H), 1.28 (s, 2 H); ^{13}C NMR (benzene-d_6, 22.5 MHz) δ 100.1 (d), 96.1 (d), 82.5 (d), 40.0 (d), 31.3 (?).

***(endo*-9-Bromobicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum.** A 100-mL round-bottomed flask containing (diglyme)tricarbonylmolybdenum (3.50 g, 11.15 mmol) was equipped with a size D filter frit and a straight gas line adaptor, in a drybox. A suspension of (diglyme)tricarbonylmolybdenum in 15 mL of THF was prepared at −78 °C. To this suspension was added *endo*-9-bromobicyclo[6.1.0]nona-2,4,6-triene (2.74 g, 13.9 mmol) at once with a syringe under a flow of argon. The resulting solution was pumped to reflux and backfilled with argon three times. The solution was warmed to room temperature and stirred for 4 h. The THF was removed, and 80 mL of diethyl ether was added by vacuum transfer. The solid material was extracted with the refluxing ether. The warm ether solution was filtered and cooled to −78 °C. The cold ether solution was back-filtered, and the extraction procedure was repeated two more times. After the last extraction, the resulting yellow solid was washed with 30 mL of hexane at −78 °C. After being dried under vacuum, a yellow solid (2.23 g, 5.92 mmol) was isolated in a yield for 53.1%. The presence of two isomers in a ratio of 18.4:1 was indicated by the NMR data.

Major isomer: ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 5.89 (s, 2 H), 5.28 (d, J = 9.3 Hz, 2 H), 4.31 (d, J = 9.3 Hz, 2 H), (t, J = 5.3 Hz, 1 H), 2.24 (d, 1 H); ^{1}H NMR (benzene-d_6, 300 MHz) δ 5.37 (s, 2 H), 4.74 (d, 2 H), 3.72 (d, 2 H), 3.01 (t, 1 H), 1.18 (d, 2 H); ^{13}C{^{1}H} (benzene-d_6, 22.5 MHz) δ 229.4, 217.5, 131.3, 101.9, 99.9, 43.7, 18.2.

Minor isomer: ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 5.78 (dd, J = 2.5, 4.9 Hz, 2 H), 5.59 (ddd, J = 2.5, 4.8, 10.3 Hz, 2 H), 4.57 (d, J = 10.3 Hz, 2 H), 3.09 (t, J = 7.6 Hz, 1 H), 1.35 (d, J = 7.6 Hz, 2 H); ^{1}H NMR (benzene-d_6, 300 MHz) δ 4.75–4.90 (m, 4 H), 4.12 (d, 2 H), 2.42 (t, 1 H), 0.56 (d, 2 H); ^{13}C{^{1}H} NMR (benzene-d_6, 22.5 MHz) δ 99.0, 97.8, 84.4, 27.0, 26.05.

(Bicyclo[6.1.0]nona-2,4,6-triene-*1,8-d*$_2$)tricarbonylchromium. A suspension of chromium hexacarbonyl (250 mg, 1.10 mmol) in 15 mL of acetonitrile was prepared in a two-neck 25-mL round-bottomed flask equipped with a size D filter frit and gas inlet adapter. After the solution was refluxed for 18 h, the acetonitrile was removed under vacuum, leaving a yellow solid. To this solid was added 10 mL of THF. To the resulting suspension stirring at 0 °C was added bicyclo[6.1.0]nona-2,4,6-triene-*1,8-d*$_2$ (200 mg, 1.70 mmol, 80% deuterium) with a syringe through the gas line inlet adapter under a flow of argon. The solution was warmed to room temperature and stirred overnight. The THF was removed from the red solution under vacuum, and 10 mL of hexane was added. The hexane was heated to reflux, cooled to room temperature, and filtered. The clear red solution was concentrated to 2 mL and cooled to −78 °C. The cold solution was filtered; the red orange product was dried under vacuum. After sublimation at 85–95 °C at 0.001 mmHg, the desired complex (45 mg, 0.18 mmol) was obtained in a yield of 16%: ^{1}H NMR (C_6D_{12}, 300 MHz, normalized to 8.4 H) δ 5.67 (dd, 2.04 ± 0.02 H), 5.18 (ddd, 1.99 ± 0.02 H), 4.63 (d, 1.99 ± 0.02 H), 0.92 (m, 0.41 ± 0.02 H), 0.67 and 0.62 (m, 1.98 ± 0.03 H).

Tris(dimethylformamide)tricarbonyltungsten. $(DMF)_3W(CO)_3$ was prepared by the method of Salzer.[5]

(Bicyclo[6.1.0]nona-2,4,6-triene)tricarbonyltungsten. (Bicyclo[6.1.0]nona-2,4,6-triene)tricarbonyltungsten was prepared by a method similar to that of Salzer.[5] A two-neck 25-mL round-bottomed flask containing $(DMF)_3W(CO)_3$, (750 mg, 1.5 mmol) was equipped with a size D filter frit and a straight gas line adapter, in a drybox. A suspension of the $(DMF)_3W(CO)_3$ in 5 mL of THF was prepared at −78 °C. To this suspension was added bicyclo[6.1.0]nona-2,4,6-triene (230 mg, 1.9 mmol) at once with a syringe through the gas line adapter. The solution was pumped to reflux and backfilled with argon three times. The solution was heated for 5 h in a 44 °C oil bath. After the THF was removed under vacuum, the product was extracted into 20 mL of refluxing hexane. The hot solution was filtered and concentrated to 7 mL. The solution was cooled to −78 °C and back-filtered. The resulting orange-red solid was dried under vacuum to give the product (150 mg, 0.39 mmol) in a yield of 20.5%: ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 5.90 (dd, J = 5.0, 2.5 Hz, 2 H), 5.39 (ddd, 2 H), 4.74 (bd, 2 H), 1.09 (dd, J = 4.9, 8.2 Hz, 2 H), 0.69 (td, 1 H), 0.21 (td, 1 H).

General Procedure for NMR-Tube-Scale Rearrangements. All NMR tubes were washed with NH_4OH for a minimum of 2 days and oven-dried for an additional 2 days. The tubes were charged with a 0.5-mL solution of the appropriate compound in either cyclohexane or cyclohexane-d_{12}, in a drybox. The tubes were sealed under vacuum after five freeze/pump/thaw cycles at 10^{-6} torr.

General Procedure for Large Scale Rearrangements. Pyrex tubes (19 cm, 1.3-cm o.d., 1.0-cm i.d.) were NH_4OH washed for 2 days and oven-dried for an additional 2 days. A cyclohexane solution of the appropriate compound was prepared in a drybox. Five milliliter aliquots of the solution was transferred with a syringe into the appropriate number of the above tubes. The tubes were kept in the drybox until they were sealed. The tubes were sealed under vacuum after five freeze/pump/thaw cycles at 10^{-6} torr. The tubes were 11 cm in length after being sealed. After the reaction was complete, the tubes were opened in the air and quickly filtered through a syringe filter using 0.45-μm Teflon filters with a glass fiber prefilter. The cyclohexane was immediately removed under vacuum. NMR spectra of the complexes were obtained without any further purification.

When NMR spectra of the noncomplexed olefins were required, the olefins were removed from the metal by using diethylenetriamine. The complex was dissolved in 25 mL of isopentane, and the resulting solution was treated with an excess of diethylenetriamine. After being stirred for approximately 15 min, the orange solution became a milky white color. The solution was washed three times with 10 mL of water and dried over $MgSO_4$. The solution was filtered through a small plug of silica, and the isopentane was carefully removed at 120–140 mmHg from an ice bath.

General Procedure for Measuring the Kinetics of Rearrangement of (Bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum and Derivatives. A solution of (bicyclo[6.1.0]-nona-2,4,6-triene)tricarbonylmolybdenum (or derivative) and sublimed ferrocene, to serve as a reference, in C_6D_{12} was prepared in a drybox. The solution was filtered through a 0.45-μm Teflon membrane syringe filter, and 0.5-mL portions of the solution were added to NH_4OH-washed oven-dried NMR tubes. The tubes were sealed under vacuum after five freeze/pump/thaw cycles at 10^{-6} torr. The reaction was quenched by putting the tubes in an ice bath after being removed from the kinetics bath. The ratio of starting material to ferrocene was obtained by measuring the integral of the δ 4.60 peak from H_2 and H_7 in the complex under study and the integral of the ferrocene peak, δ 4.05.

X-ray Structure of (Bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum. A sample of (bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum was purified by recrystallization from hexane, followed by two sublimations at 90 °C and 0.001

mmHg. A saturated solution of the complex in hexane at reflux under an argon atmosphere was allowed to cool to room temperature. The solution was filtered to remove any solid which formed upon cooling. After the solution was standing overnight at room temperature, the crystals that had formed were collected by filtration. A cubic-shaped crystal, roughly 0.3 mm on an edge, was sealed in a Lindemann capillary. Preliminary X-ray photographs displayed orthorhombic symmetry. Precise lattice constants, determined from a least-squares fit of 15 diffractometer-measured 2θ values are $a = 14.185$ (1), $b = 10.417$ (1), and $c = 7.230$ (1) Å. The cell volume is 1068.3 Å^3, with four molecules per unit cell, giving a calculated density of 1.85 g/cm^3 and linear absorption coefficient of 101.5 cm^{-1} (for Cu Kα). Systematic absences ($0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$) were consistent with space groups $Pnma$ and $Pn2_1a$. Structure solution and refinement confirmed the choice of centrosymmetric space group $Pnma$ over noncentrosymmetric space group $Pn2_1a$. The asymmetric unit is composed of $MoC_7O_2H_6$, with the molecule using a crystallographic mirror plane. All unique diffraction maxima with $2\theta < 114°$ and $128° < 2\theta < 156°$ were measured on a four-circle, computer-controlled diffractometer with a variable-speed, 1° ω scan, using graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å). After correction for Lorentz, polarization, and background effects, 756 out of 1143 reflections were judged observed ($|F| \geq 3\sigma(|F|)$). The data were not corrected for absorption or extinction effects. A Patterson synthesis revealed the Mo atom position and the non-hydrogen light atoms were located in successive ΔF maps. Hydrogen atoms were included at calculated positions. Block-diagonal least-squares refinement of 10 anisotropic non-hydrogen atoms and 6 fixed hydrogen atoms converged to $R = 0.115$ ($R = (\sum||F_o| - |F_c||)/\sum|F_o|$) and $R_w = 0.137$ ($R_w = [(\sum w(|F_o| - |F_c|)\sum|F_o|^2)^{1/2}$). A final difference electron density map showed no evidence of disorder or the presence of solvent molecules.

X-ray Crystal Structure of (*endo*-9-Bromobicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum. A near saturated solution of the complex in diethyl ether was prepared. This solution was sealed under vacuum in a 15-mL glass ampule. The solution was slowly cooled from 10 to −60 °C over 3 days. The crystals were collected and dried under vacuum. A single crystal with approximate dimensions 0.2 × 0.2 × 0.3 mm was sealed in a Lindemann capillary. Preliminary X-ray photographs displayed monoclinic symmetry. Precise lattice constants, determined from a least-squares fit of 15 diffractometer-measured 2θ values, are $a = 8.740$ (1), $b = 10.038$ (1), and $c = 13.742$ (1) Å and $\beta = 85.900$ (9)°. The cell volume is 1202.5 Å^3, with four molecules per unit cell, giving a calculated density of 2.08 g/cm^3 and linear absorption coefficient of 130.0 cm^{-1} (for Cu Kα). The one systematic absence ($0k0$, $k = 2n + 1$) was consistent with space groups $P2_1$ and $p2_1/m$. Structure refinement confirmed the choice of centrosymmetric space group $P2_1/m$ over noncentrosymmetric space group $P2_1$. The asymmetric unit is composed of $Mo_2C_{14}O_{10}Br_2$, with two independent molecules using a crystallographic mirror plane. All unique diffraction maxima with $2\theta < 114°$ were measured on a four-circle, computer-controlled diffractometer with a variable-speed, 1° ω scan, using graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å). After correction for Lorentz, polarization, and background effects, 1494 out of 1736 reflections were judged observed ($|F| \geq 3\sigma(|F|)$). The data were not corrected for absorption or extinction effects. A Patterson synthesis revealed the Mo atom positions, and the non-hydrogen light atoms were located in successive ΔF maps. Hydrogen atoms were included at calculated positions. Block-diagonal least-squares refinement of 22 anisotropic non-hydrogen atoms and 10 fixed hydrogen atoms converged to $R = 0.068$ ($R = (\sum||F_o| - |F_c||)/\sum|F_o|$) and $R_w = 0.077$ ($R_w = [(\sum w(|F_o| - |F_c|)\sum|F_o|^2)]^{1/2}$). A final difference electron density map showed no evidence of disorder or the presence of solvent molecules.

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Supplementary Material Available: Tables of crystal data, fractional coordinates, anisotropic thermal parameters, interatomic distances, interatomic angles, and torsional angles for (bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum and (*endo*-9-bromobicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum (12 pages); listings of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.