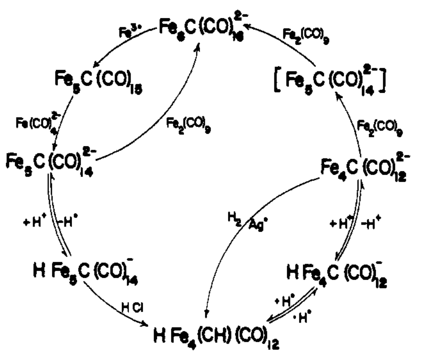
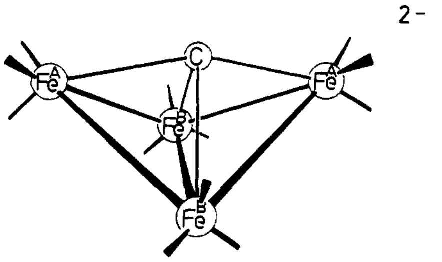


Figure 1. This cyclic scheme summarizes the demonstrated relationships among the Fe_4C and Fe_5C carbonyl systems.

form **2** with a hydride bridging between the two basal, Fe^B, iron atoms. There were similarities between the carbonyl ^{13}C DNMR spectra of the monoanion with those of $HFe_4(\eta^2\text{-}CH)(CO)_{12}$; carbonyl site exchange barriers increase in the series $[Fe_4C(CO)_{12}{}^{2-}] < [HFe_4C(CO)_{12}{}^-] < HFe_4(\eta^2\text{-}CH)(CO)_{12}$. Intermolecular exchange of H between $HFe_4(CH)(CO)_{12}$ and $HFe_4C(CO)_{12}{}^-$ was not observable on the NMR time scale. Single crystals of salts of the two cluster carbide anions are under crystallographic study.



Protonation of the exposed, four-coordinate carbide carbon atom in $[HFe_4(\mu_4\text{-}C)(CO)_{12}{}^-]$ is fast and represents the first protonation of an exposed carbide carbon atom in a metal cluster. The five-coordinate carbon atom in $Fe_5(\mu_5\text{-}C)(CO)_{15}$ is not protonated by strong acids, although the generation of $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ by reaction of $[Fe_5C(CO)_{14}{}^{2-}]$ with HCl must involve at some step transfer of hydrogen to the carbide carbon atom. In addition, $[Fe_4C(CO)_{12}{}^{2-}]$ undergoes framework expansion when allowed to react with mononuclear transition metal complexes. The previously[1] reported $[RhFe_4C(CO)_{14}{}^-]$ was obtained from the reaction of the dianion with $[Rh(CO)_2Cl]_2$, and a new octahedral carbide, $[Mo_2Fe_4C(CO)_{18}{}^{2-}]$, was formed with $Mo(CO)_3(THF)_3$. Cyclic interconversions in the Fe_4C and Fe_5C systems are summarized in Figure 1.

Oxidation of $Fe_4C(CO)_{12}{}^{2-}$ with $AgBF_4$ in the presence of H_2 and of D_2, respectively, yielded $HFe_4(CH)(CO)_{12}$ and $DFe_4(CD)(CO)_{12}$ implicating oxidative addition of hydrogen to a coordinately unsaturated $Fe_4C(CO)_{12}$ intermediate. This is the first facile H_2 reduction of a carbide carbon atom in metal cluster chemistry and is a formal analogue of a step proposed[3,5] in Fischer-Tropsch reactions.

Acknowledgments. Support of this research by the National Science Foundation is gratefully acknowledged as is the assistance of Mr. Robert R. Burch in the NMR studies.

References and Notes

(1) Preceeding paper in this series: M. Tachikawa and E. L. Muettertles, *J. Am. Chem. Soc.*, **102**, 1725 (1980).
(2) M. Tachikawa and E. L. Muetterties, *Prog. Inorg. Chem.*, in press (a comprehensive review of metal carbide clusters).
(3) E. L. Muettertles and J. Stein, *Chem. Rev.*, **79**, 479 (1979).
(4) E. L. Muetterties, *J. Organomet. Chem.*, in press.
(5) Carbide-like carbon atoms are postulated to be intermediates in Fischer–Tropsch reactions effected by metal surfaces like Fe, Ru, and Co.[3] The surface carbides, which are likely to have relatively low metal atom coordination numbers, react with hydrogen at 25 °C to form hydrocarbons. See discussion and references to original literature in ref 3.
(6) A Schlenk flask (500 mL) which contained a suspension of $[(C_2H_5)_4N]_2[Fe_5C(CO)_{14}]$ (500 mg) in 30 mL of toluene was filled with hydrogen chloride to give a rapid formation of an oily layer of $[(C_2H_5)_4N][HFe_5C(CO)_{14}]$. Vigorous stirring was maintained for 24 h. A white solid separated. The solution phase was evaporated to give black, crystalline $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ (236 mg, 98% yield).
(7) This cluster after recrystallization from hexane analyzed for $[HFe_4(\eta^2\text{-}CH)(CO)_{12}]$. Anal. Calcd for $C_{13}H_2Fe_4O_{12}$: C, 27.22; H, 0.18; Fe, 38.95. Found: C, 27.38; H, 0.36; Fe, 39.2. Mass spectrum (crystals from hexane): 574 (parent), 546 (P − CO), 518 (P − 2CO), 490 (P − 3CO), 462 (P − 4CO), 434 (P − 5CO), 406 (P − 6CO), 378 (P − 7CO), 350 (P − 8CO), 322 (P − 9CO), 294 (P − 10CO), 266 (P − 11CO), 236 (P − 12CO − 2H). IR (hexane solution): ν_{CO} 2099 (vw), 2053 (vs), 2036 (s), 2031 (m), 2015 (sh), 1987 (m).
(8) ^{13}C satellites were observed for a saturated dichloromethane solution of the cluster. When the cluster was prepared from ^{13}CO-enriched $Fe_5C(CO)_{14}{}^{2-}$, there was no enhancement of the CH ^{13}C satellite intensity establishing that the CH carbon atom is not derived from a carbonyl carbon in the synthesis step.
(9) Irradiation of the δ −27.95 resonance at 35 and 65 °C resulted in an intensity from the −1.31 resonance that was 65 and 6%, respectively, relative to the intensity in the absence of the irradiation.
(10) Integration of the C–H and Fe_x–H resonances for a mixture of $HFe_4(CH)(CO)_{12}$, $HDFe_3C(CO)_{12}$, and $DFe_4(CD)(CO)_{12}$ (ratios determined by mass spectrometry) yielded a ratio of $HFe_4(CD)(CO)_{12}$ to $DFe_4(CH)(CO)_{12}$ of 1.73 at 35 °C.
(11) (a) R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, **100,** 7726 (1978); (b) R. B. Calvert, J. R. Shapley, A. J. Schultz, J. M. Williams, S. L. Sulb, and G. D. Stucky, *Ibid.*, **100,** 6240 (1978).
(12) J. M. Williams, R. K. Brown, A. J. Schultz, G. D. Stucky, and S. D. Ittel, *J. Am. Chem. Soc.*, **100,** 7407 (1978).
(13) An isoelectronic and isostructural cluster is $HFe_4(\eta^2\text{-}CO)(CO)_{12}{}^-$; cf. M. Manassero, M. Sansoni, and G. Longoni, *J. Chem. Soc., Chem. Commun.*, 919 (1976).
(14) M. A. Beno, J. M. Williams, M. Tachikawa, and E. L. Muetterties, *J. Am. Chem. Soc.*, following paper in this issue.
(15) (a) D. Seyferth, *Adv. Organomet. Chem.*, **14,** 97 (1976); (b) R. B. Calvert and J. R. Shapley, *J. Am. Chem. Soc.*, **99,** 5225 (1977).
(16) EHMO calculations for CH on a Ni(111) surface suggest that the system energy is reduced in going from a μ_3-CH binding with the CH vector normal to the surface to a η^2-CH binding with both the carbon and the hydrogen atoms bound to surface nickel atoms (R. M. Gavin and E. L. Muetterties, unpublished calculations). In addition, J. E. Demuth and H. Ibach, *Surf. Sci.*, **78,** L238 (1978), propose on the basis of spectroscopic data that chemisorbed CH on Ni(111) does not have the CH vector normal to the surface.
(17) (a) Anal. Calcd for $(PPN^+)_2[Fe_4C(CO)_{12}{}^{2-}]$: C, 61.92; H, 3.67; N, 1.70. Found: C, 61.12; H, 3.74; N, 1.70. IR (dichloromethane): ν_{CO} 2003 (w), 1968 (s), 1942 (vs), 1912 (m). ^{13}C NMR (CH_2Cl_2, 20 °C, 45.3 MHz): 220.8 (6) and 222.8 (6) ppm for carbonyl carbon atoms. (b) Anal. Calcd for $[PPN^+][HFe_4C(CO)_{12}{}^-]$: C, 52.97; H, 2.81; N, 1.26. Found: C, 52.91; H, 2.89; N, 1.27. IR (CH_2Cl_2): ν_{CO} 2010 (s, sh), 2005 (vs), 1987 (s), 1978 (*m*, sh), 1927 (w). ^1H NMR (CD_2Cl_2, 20 °C, 180 MHz): hydride at −26.8 ppm ($\omega_{1/2}$ = 30.3 Hz).
(18) Low barriers to CO site exchange localized on single metal sites is common in metal clusters: E. Band and E. L. Muetterties, *Chem. Rev.*, **78**, 639 (1978).

M. Tachikawa, E. L. Muetterties*
Department of Chemistry, University of California
Berkeley, California 94720

Received February 1, 1980

Fischer–Tropsch Chemistry: Structure of a Seminal η^2-CH Cluster Derivative, $HFe_4(\eta^2\text{-}CH)(CO)_{12}$

Sir:

We have completed a high-precision low-temperature [−100 (3) °C] X-ray crystal structure study of a Fe_4 "butterfly" cluster containing an unusual η^2-CH ligand. This cluster,[1] $HFe_4(\eta^2\text{-}CH)(CO)_{12}$, **1,** occupies a central role in transformations that document the proposed[2] high reactivity of low-coordinate carbon (carbide) ligands in clusters and that *formally* may relate to intermediates[3] in some metal surface catalyzed Fischer-Tropsch reactions.[4-6]

After collection of an extensive low temperature data set[7] for crystals of **1** recrystallized from hexane, the structure was solved using MULTAN.[8] There is a butterfly array of four iron atoms, each with three terminal carbonyl ligands, with the carbidic carbon atom nestled near the center of the top of the "wings" of the Fe_4 array where it forms a strong C–H–Fe interaction as depicted in Figure 1.[9] The most striking feature

0002-7863/80/1502-4542$01.00/0

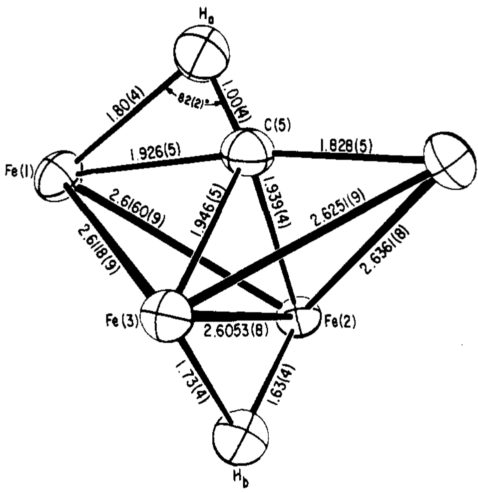
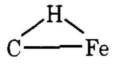


Figure 1. Atom labeling scheme for [$HFe_4(\eta^2\text{-}CH)(CO)_{12}$] with the carbonyl groups omitted for clarity. The labeling scheme is the same as that used by Manassero et al.[11] Only one of the two independent molecules which occupy the asymmetric unit is shown (the two molecules are essentially identical within experimental error). The cluster nearly possesses a noncrystallographic mirror plane passing through Fe(1), Fe(4), C(5), H$_a$, and H$_b$ and bisecting the Fe(2)–Fe(3) bond.

of the structure is that the C–H ligand is an η^2 ligand with a three-center interaction (A).[1] The hydridic hydrogen atom



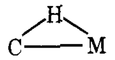
A

(H$_b$) bridges Fe(2) and Fe(3), and, despite this bridging ligand, the Fe(2)–Fe(3) separation does not differ substantially from the other Fe–Fe bonds.[10] In this bridging hydride, the Fe(2) and Fe(3) to H$_b$ distances of 1.63 (4) and 1.73 (4) Å, respectively, agree within 2σ and agree with an expected Fe–H$_b$ X-ray distance of ~1.7 Å.

There are two related Fe_4C butterfly structures namely the 62-electron[11] [$HFe_4(\eta^2\text{-}CO)(CO)_{12}^-$], **2,** and 60-electron[12a] [$Fe_4(CCOOCH_3)(CO)_{12}^-$], **3,** cluster. The average iron-iron bonding distance in **1** is 2.619 (5) Å which is similar to the average value[11] of 2.627 (5) Å for the other 62-electron cluster, **2,** and disparate with respect to the expectedly shorter distances in the electron-deficient cluster, **3,** where the range is 2.430–2.553 Å.[12]

Iron-carbon skeletal distances in **1** are of two types. There is a set of three which averages to 1.937 (7) Å and a unique short distance of 1.828 (5) Å. The latter is the apical Fe(4)–C(5) edge distance opposite to the multicenter bond (see A). Significantly, the former set of three coincides closely with the values of Fe–C multicenter bonds in neutral iron carbide clusters (~1.89–1.95 Å).[2] The pattern of three longer Fe–C and one unique, shorter distance is also evident in the isoelectronic cluster, [$HFe_4(\eta^2\text{-}CO)(CO)_{12}^-$], **2.** For **1,** the dihedral angle defined by the Fe(1)–Fe(3)–Fe(2) and Fe(3)–Fe(2)–Fe(4) planes is 110.6°, a value close to that of 117° found[11] in the isoelectronic [$HFe_4(\eta^2\text{-}CO)(CO)_{12}^-$] cluster, **2.** The dihedral angle in the electron-deficient cluster, **3,** is quite different, 130°.[12] Clearly, clusters **1** and **2** are not only isoelectronic but closely isostructural in a quantitative context.[13] In addition, the spatial arrangement of the 12 carbonyl ligands in **1** conforms closely to that in the isoelectronic carbonyl derivative, **2,** insofar as can be determined from the published data for the latter.[11] All 12 carbonyl ligands are terminally bound, three to each iron atom, and the C–O distances are in the normal range of 1.125 (5) to 1.151 (6) Å. Overall, the spatial arrangement of the carbonyl groups appears to minimize nonbonded interactions; the closest nonbonded separations among the C and O atoms of the carbonyl groups are greater than 2.8 Å.

In the polydentate C–H group, the structural parameters incisively identify a closed[14] three-center unit (A). The Fe–C separation of 1.926 (5) Å establishes a C–H–Fe bonding interaction in which the overlap integral for C–Fe is substantial. Other crystallographically defined examples of C (alkyl or aromatic)–H–metal multicenter interaction in mononuclear metal complexes have much larger carbon-metal atom separations with a range of 2.36–3.32 Å.[15] The only other tight interaction (B) established was that for a dinuclear tantalum



B

neopentylidene complex where the Ta–C distance was 1.898 (2) Å.[15] The complimentary C–H and H–Fe overlaps in the multicenter bond (see A) of **1** must be considered significant even though the C–H and H–Fe distances of 1.00 (5) and 1.80 (4) Å, respectively, may be in error by as much as 0.1–0.2 Å. These C–H and H–Fe distances may be compared with those of a mononuclear iron complex with a multicenter C (alkyl C–H)–H–Fe interaction accurately determined in a neutron crystallographic investigation[16] of {$\eta^3\text{-}C_8H_{13}Fe[P(OCH_3)_3]_3^+$}$BF_4^-$, **4.** In **4,** the C–H, H–Fe, and C–Fe distances are 1.164 (3), 1.874 (3), and 2.36 (2) Å, respectively. Other crystallographically defined C–H···M interactions in mononuclear complexes are much longer than the value of 1.874 Å for this iron phosphite complex.[15] Thus, our studies establish for the first time a strong η^2 binding of a methylidyne ligand; all previously described methylidyne or alkylidyne clusters have $\mu_x\text{-}\eta^1$-CR (x = 2,[17a] 3,[17b,c] 4[17d]) stereochemistry as in the well-known $RCCo_3(CO)_9$ system.[17b] Our results are significant with respect to the formal cluster-surface analogy because the binding of CH at the characteristically coordinately unsaturated metal surface should be η^2 in character[18,19] and because the C–H chemisorption state on Ni(111) has been interpreted in terms of the C–H vector being tilted with respect to the surface normal.[20] Also, we anticipate other isoelectronic and isostructural members in this η^2-ligand 62-electron cluster series, e.g., [$HFe_4(\eta^2\text{-}CN)(CO)_{12}^{2-}$] and [$HFe_4(\eta^2\text{-}NH)(CO)_{12}^+$], and are attempting their synthesis.

Acknowledgments. The work at Argonne National Laboratory is sponsored by the Office of Basic Energy Sciences of the U.S. Department of Energy. This collaborative research is also funded in part by the National Science Foundation (Grant CHE-78-20698) to J.M.W. and E.L.M. and (Grant CHE-79-03933) to E.L.M.

Supplementary Material Available: A listing of positional and thermal parameters derived from full-matrix least-square refinement (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) M. Tachikawa and E. L. Muetterties, *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) M. Tachikawa and E. L. Muetterties, *Prog. Inorg. Chem.*, in press.
(3) E. L. Muetterties and J. Stein, *Chem. Rev.*, **79,** 479 (1979).
(4) G. Low and A. Bell, *J. Catal.*, **57,** 397 (1979).
(5) P. Biloen, J. N. Helle, and W. H. M. Sachtler, *J. Catal.*, **58,** 95 (1979).
(6) J. A. Rabo, A. P. Risch, and M. L. Poutsma, *J. Catal.*, **53,** 295 (1978).
(7) Crystals of $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ are monoclinic with space group $P2_1/c$ (C_{2h}^5, No. 14). Using 18 automatically centered reflections (Syntex $P2_1$ diffractometer, graphite monochromator and Mo Kα radiation, λ = 0.71069 Å) at T = −100 (3) °C, we obtained lattice constants of a = 8.775 (2), b = 33.18 (1), c = 13.894 (5) Å; β = 113.10 (2)°; V = 3720 (2) Å^3; Z = 8; ρ_{obsd} = 1.94, ρ_{calcd} = 2.05 g cm^{-3}. A total of 9290 replicate data were collected (4.0° ≤ 2θ ≤ 50.0°) and averaged ($R[F_{av}]$ = 0.018) to yield 5947 unique reflections of which 4625 had $F^2 \geq 3\sigma F_o^2$. Data were corrected in the normal fashion, including individual absorption corrections (μ_c = 32.0 cm^{-1}) and transmission factors ranged from 0.44 to 0.55. After the structure was solved using MULTAN,[8] the two hydrogen atoms were located in difference

Fourier maps. Full-matrix least-squares refinement (anisotropic temperature factors for all atoms except hydrogen which were treated isotropically) yielded $R(F_o) = 0.057$ (all data). Form factors for Fe, C, and O (and anomalous dispersion corrections for Fe) were taken from the International Tables, Vol. III, Kynoch Press, Birmingham, England, 1962, pp 202–203, and from Vol. IV, pp 149–50, respectively. The H atom form factors were from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42,** 3175 (1965). Two data sets were collected at −100 °C on two *different* crystals. The first data set contained 3225 unique data only and was used to solve the structure while a much more extensive data set was collected on a smaller crystal with less absorption. Although the derived positional parameters for all atoms are the same for both data sets within the estimated standard deviations, only those for the second data set are given because of the expectedly higher precision.

(8) G. Germain, P. Main, and M. M. Wolfson, *Acta Crystallogr.*, **19,** 1014 (1965).

(9) The iron atom labeling scheme used in the figure is identical with that used by Manassero et al.[11] for $[HFe_4(\eta^2\text{-}CO)(CO)_{12}^-]$.

(10) Normally a single H bridge tends to increase the metal–metal separation but in this cluster the unique carbon is a bridging atom that counterbalances this effect.

(11) M. Manassero, M. Sansoni, and G. Longoni, *J. Chem. Soc., Chem. Commun.*, 919 (1976).

(12) (a) J. S. Bradley, G. B. Ansell, and W. E. Hill, *J. Am. Chem. Soc.*, **101,** 7417 (1979). (b) No error estimates were reported.

(13) A 62-electron four-metal atom cluster should generally have a butterfly arrangement; cf. J. W. Lauher, *J. Am. Chem. Soc.*, **100,** 5305 (1978).

(14) Cf. W. N. Lipscomb, "Boron Hydrides," E. L. Muetterties, Ed., Academic Press, New York, 1975, Chapter 2 and references therein.

(15) See references to and discussion of C–H ⋯ M interactions in mono- and dinuclear metal complexes in ref 16.

(16) R. K. Brown, J. M. Williams, A. J. Schultz, G. D. Stucky, S. D. Ittel, and R. L. Harlow, *J. Am. Chem. Soc.*, **102,** 981 (1980).

(17) (a) M. Nitay, W. Priester, and M. Rosenblum, *J. Am. Chem. Soc.*, **100,** 3620 (1978); (b) D. Seyferth, *Adv. Organomet. Chem.*, **14,** 98 (1976), and references therein; (c) for example, see G. M. Sheldrick and J. P. Yesinowski, *J. Chem. Soc.*, Dalton, *Trans.*, 873 (1975), and S. Aime, L. Milone, E. Sappa, and A. Tiripicchio, *ibid.*, 227 (1977). (d) C. R. Eady, J. M. Fernandez, B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 421 (1978).

(18) Preliminary EHMO calculations for C–H bonding on a Ni(111) surface indicate an energy decrease in changing from a μ_3-CH binding with the C–H vector normal to the surface to an η^2-CH binding with carbon and hydrogen bound to surface nickel atoms: R. M. Gavin and E. L. Muetterties, unpublished work.

(19) A μ-η^2-CH binding should appear often for clusters if the cluster were coordinately unsaturated *without* the C–H–M multicenter 2-electron interaction.

(20) J. E. Demuth and H. Ibach, *Surf. Sci.*, **78,** L 238 (1978).

Mark A. Beno, Jack M. Williams*
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439

M. Tachikawa, E. L. Muetterties*
Department of Chemistry, University of California
Berkeley, California 94720

Received March 7, 1980

Applications of Bridgehead Alkenes to Organic Synthesis. Regio- and Stereochemical Control in the Diels–Alder Route to Polyfunctional Cyclohexenes and Cyclohexanes

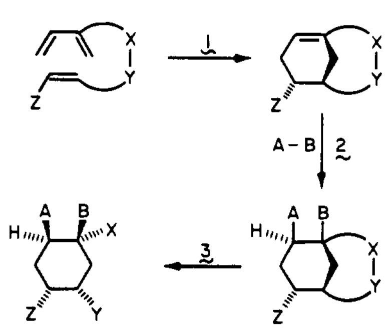
Sir:

Suitably functionalized bicyclic molecules occupy an important role in synthetic organic chemistry. The well-defined stereochemical relationship of the carbon framework permits simultaneous control over the relative configuration of a number of asymmetric centers. The stereochemical information contained in these bicyclic molecules can be retrieved in a subsequent fragmentation or cleavage reaction.

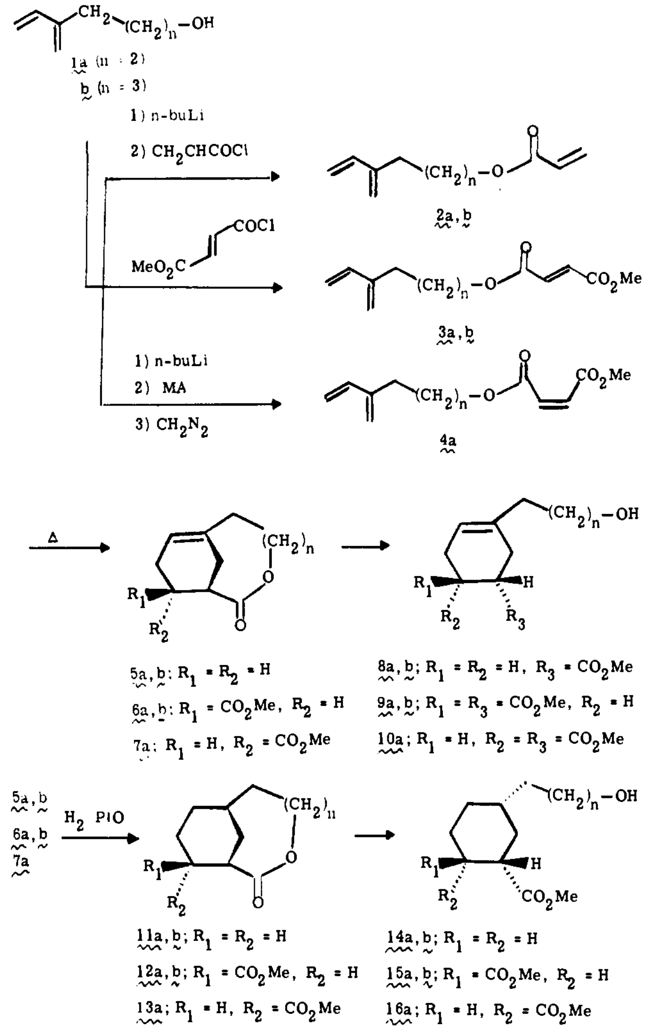
We report herein an application of this methodology to control stereo- and regiochemistry in the synthesis of polysubstituted cyclohexenes and cyclohexanes.

Our approach is outlined in Scheme I. A key step in the synthesis is an intramolecular Diels–Alder reaction that results in formation of a medium-ring bicyclic lactone containing a *bridgehead double bond.*[1] We illustrate, for the first time, the utility of bridgehead alkanes in organic synthesis by the addition–cleavage sequence shown in steps 2 and 3 in Scheme I. The addition step establishes the relative configuration of three asymmetric centers; cleavage of the original linkage between diene and dienophile results in formation of a di-, tri-, or tetrasubstituted cyclohexane with control over all asymmetric centers.

Scheme I



Scheme II



The specific compounds used to illustrate this sequence are the triene esters **2–4,** chosen because of the ease of cleavage of the lactone bridge and the activating influence of the carbonyl group in the intramolecular Diels–Alder step.[2,3]

Esterification of dienols **1a**[4] and **1b**[5] by the methods outlined in Scheme II results in 40–60% yields of triene esters **2–4.**[6] Intramolecular cycloaddition was accomplished by heating 0.1 M solutions in xylene. Cycloadditions were complete in 5–6 h. Typical reaction conditions: 185 °C for **2a, 2b,** and **4a,** and 130 °C for **3a** and **3b.** The bridgehead alkenes (**5–7**), formed in 40–60% yield, are sufficiently stable to allow isolation by

0002-7863/80/1502-4544$01.00/0