the further conversion of products. Anal. Calcd for $C_{42}H_{60}O_6FeK_3$: C, 60.48; H, 7.25. Found: C, 60.59; H, 7.53.

Synthesis and Reaction of K[Fe(DTBC)(bipy)(OH)$_2$]·C_2H_5OH. The degassed aqueous solution of $FeCl_3$ (8 cm^3, 0.324 g, 2.00 mmol) was added dropwise to 10 cm^3 of the degassed 50% aqueous ethanol solution containing **1** (0.445 g, 2.00 mmol), bipyridine (0.312 g, 2.00 mmol), and KOH (0.56 g, 10 mmol) and stirred at room temperature for 0.5 h. Dark violet precipitates which were formed were filtered under Ar, washed thoroughly with degassed water, and dried for 3 h at 60 °C under vacuum. The absence of Cl was shown by the elemental analysis. Although the elemental analysis was slightly above acceptable limits, the content of the DTBC ligand was estimated from the total yield of **1** and **2** formed by the decomposition of the complex with 2 N HCl and indicated the ratio of Fe:DTBC = 1:1. Reactions of the complex (0.030 g, 0.05 mmol) with O_2 and $O_2^{-\bullet}$ were performed under the same conditions as the above two cases except the addition of KO_2 (0.004 g, 0.05 mmol) and 18-crown-6 (0.012 g, 0.05 mmol). Product analysis was worked up as described above. Anal. Calcd for $C_{28}H_{42}N_2O_6FeK$: C, 56.62; H, 6.58; N, 5.08; Fe, 10.12. Found: C, 57.49; H, 6.54; N, 4.62; Fe, 10.45 (the Fe content was estimated by the EDTA titration at pH 1.8 after decomposition of the complex).

Oxygenation of 3,5-Di-*tert*-butyl-1,2-benzoquinone (2) in the Presence of 2,5-Di-*tert*-butyl-1,4-hydroquinone. Oxygenation of **2** (0.110 g, 0.500 mmol) was started in the presence of $FeCl_3$ (0.010 g, 0.063 mmol), bipyridine (0.029 g, 0.188 mmol), pyridine (0.45 cm^3, 6.2 mmol), and hydroquinone (0.056 g, 0.25 mmol) in THF (4.5 cm^3) at 25 °C under 1 atm O_2. After 24, 48, 72, and 96 h, 0.25 mmol of the hydroquinone was added. **2** was almost completely converted to give **3** 38%, **5** 20%, and **9** 18%. When the hydroquinone (1.00 mmol) was added all at once in the initial stage, yields of products after 24 h were 25%, 14%, and 18%, respectively, and 27% of **2** was not converted.

Measurements of Optical Spectra. Solutions of the complex (Fe = 10^{-3} – 10^{-1} mol dm^{-3}, the ratio of Fe:**1**:bipy:py was variable) were prepared in THF in an argon atmosphere at 25 °C. The reaction of the complex with oxygen was followed by measuring spectra at half an hour intervals after the atmosphere was replaced with oxygen. Spectra were recorded at room temperature on Shimadzu UV-260 and Hitachi EPS-3T instruments.

Acknowledgment. We thank the Ministry of Education for a Grant (No. 59550549). We thank Dr. Koichiro Ohshima for the measurements of GC–MS.

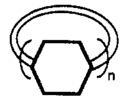
Synthesis and Chemistry of Tetracyclo[8.2.2.2^{2,5}.2^{6,9}]-1,5,9-octadecatriene

John E. McMurry,*† Gregory J. Haley,† James R. Matz,† Jon C. Clardy,† Gregory Van Duyne,† Rolf Gleiter,‡ Wolfgang Schäfer,‡ and David H. White⊥

Contribution from the Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853, Institut für Organische Chemie der Universität Heidelberg, Heidelberg, Federal Republic of Germany, and the Department of Chemistry, University of Santa Clara, Santa Clara, California 95053. *Received October 16, 1985*

Abstract: The title compound, triene **3**, was prepared by titanium-induced cyclization of the appropriate diketone precursor, and its structure was confirmed by single-crystal X-ray crystallography. Photoelectron spectroscopy indicated that little interaction was present between double bond orbitals across the ring. Electrophilic additions took place to triene **3**, not with the normal anti stereochemistry but with deep-seated skeletal rearrangement leading to formation of hexacyclic products. Epoxidation and cyclopropanation took place normally, however. The trisepoxide prepared from triene **3** proved to be extraordinarily stable to acid treatment because of the absence of any feasible reaction pathway. The monoepoxide prepared from **3** rearranged on treatment with aqueous acid to yield a hexacyclic diol. Attempted dehydrogenation of **3** also led to formation of a rearranged hexacyclic product.

Imagine a group of compounds made of *n* six-membered rings joined by double bonds at their C1 and C4 positions to form a large overall ring as in **1**. The simplest such compound, tricyclo[4.2.2.2^{2,5}]-1,5-dodecadiene (**2**), was recently reported by Wiberg,[1] but more complex members of the group had not been prepared until our recent preliminary communication on the subject.[2]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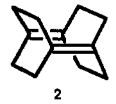
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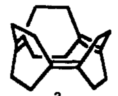
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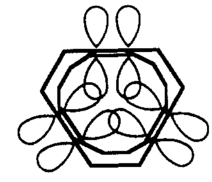
We felt that the second member of the group, tetracyclo-[8.2.2.2^{2,5}.2^{6,9}]-1,5,9-octadecatriene (**3**), might prove to be a particularly interesting compound because of its rigid structure and the unusual orientation of its three double bonds. It is possible, for example, that the double bond orbitals in **3** might exhibit a through-space interaction by ppσ overlap, leading to six-electron delocalization and consequent trishomoaromaticity,[3] as indicated in structure **4**. It is also possible that **3** might show interesting chemical reactivity because of its rigidity. For example, molecular models indicate that the interior cavity of **3** is too small to allow approach of a reagent to the inside face of the double bonds. Thus, any electrophilic-addition chemistry of **3** must occur with syn stereochemistry from the outside face of the molecule. But syn addition to one of the double bonds, as in **5**, leads to introduction of a large amount of strain according to models. Unusual chemical consequences might therefore ensue.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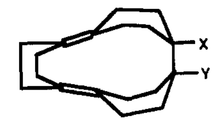
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† Cornell University.
‡ Institut für Organische Chemie der Universität Heidelberg.
⊥ University of Santa Clara.

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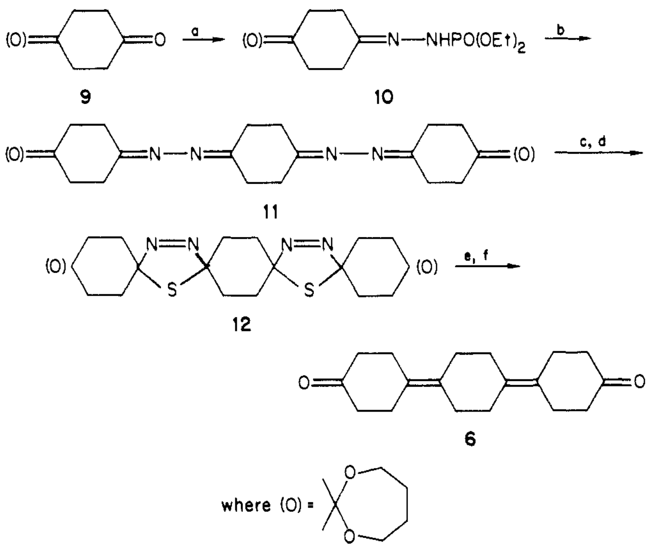
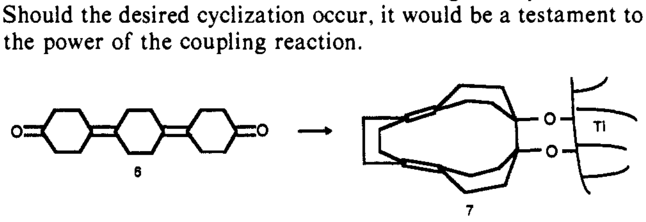
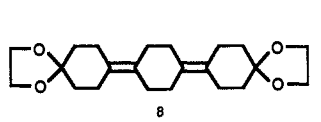
Scheme I. Synthesis of Diketone Cyclization Precursor 6



(a) $H_2NNHPO(OEt)_2$, 91%; (b) NaH, 1,4-cyclohexanedione, 81%; (c) H_2S, CH_3CN, 77%; (d) $Pb(OAc)_4$, $CaCO_3$, 63%; (e) 37% HCl, CH_2Cl_2, 97%; (f) toluene reflux, then $(EtO)_3P$, 76%.

Synthesis of Tetracyclo[8.2.2.2^{2,5}.2^{6,9}]-1,5,9-octadecatriene. The key step in our synthesis plan was to form triene **3** by an intramolecular titanium-induced cyclization of diketone **6**. Although the reductive cyclization of diketones to olefins has proven to be quite general,[4] this particular coupling was expected to provide a severe test of the reaction's limits. The major potential problem is that essentially all of the considerable strain energy in **3** is introduced during the cyclization step when the three rings must adopt near-perfect boat conformations in order to bring the two carbonyl groups within bonding distance. Furthermore, the pinacol intermediate **7** produced during the carbonyl-coupling step has exactly the unfavorable geometry referred to above, where one of the three double bond of triene **3** has undergone a syn addition. Should the desired cyclization occur, it would be a testament to the power of the coupling reaction.





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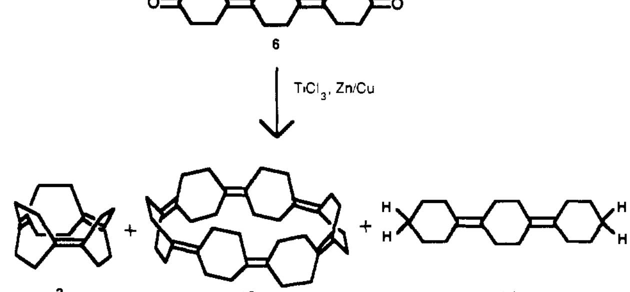
All initial attempts at the synthesis of dione **6** failed when it was discovered that bisacetal **8** and related protected diol derivatives could not be deprotected without concomitant isomerization of the acid-sensitive double bonds into the rings. Success was realized, however, when we discovered a route based on the Barton olefin synthesis,[5] whereby deprotection of the two carbonyl groups could be accomplished *prior* to introduction of the double bonds (Scheme I).

Starting from the known[6] 1,4-cyclohexanedione tetramethylene monoacetal (**9**), reaction with diethyl phosphorohydrazidate[7] gave hydrazone **10** in 91% yield. Double Horner–Emmons reaction[8] of **10** with 0.5 equiv. of 1,4-cyclohexanedione then provided bisazine **11** (81%), which was treated with excess hydrogen sulfide in acetonitrile and oxidized with lead tetraacetate to provide bisthiadiazoline **12** (97%) as a mixture of cis/trans isomers. The acetal protecting groups were then removed by treatment with aqueous hydrochloric acid in a two-phase dichloromethane/water solvent system. Reflux in toluene, followed by heating with triethyl phosphite, then effected extrusion of nitrogen and desulfurization of the intermediate thiirane to yield the desired dione **6** (76%). All synthetic intermediates were crystalline and chromatographic purification was not required at any stage. Ten-gram amounts of dione **6** could easily be prepared in a single runthrough of the scheme.

With dione **6** thus available, we examined its reaction with low-valent titanium. The reaction required much experimentation before optimum conditions were achieved, but we were ultimately able to obtain a mixture of hydrocarbon products in 90% yield. Direct vacuum sublimation of the crude reaction mixture, followed by crystallization of the sublimate from ethyl acetate, provided the desired triene **3** as a crystalline solid, mp 259–259.5 °C, in 24% yield. Chromatographic analysis of the residue indicated that the major byproducts of the reaction were diene **14** and various of its double bond isomers. In addition, a small amount of a dimeric substance that proved to be hexaene **13** could be isolated in 2.5% yield.

Structure identification of triene **3** was accomplished by ^1H and ^{13}C NMR spectroscopy. Triene **3** showed only the expected AA′BB′ multiplet at δ 2.46 (m, 12 H) and 2.01 (m, 12 H) in its ^1H NMR spectrum and only the expected two peaks at δ 129.86 and 28.43 in its ^{13}C NMR spectrum. Once pure, compound **3** proved to be stable indefinitely to air and light.



X-ray Crystal Structure of Triene 3. The structural assignment of triene **3** was confirmed by single-crystal X-ray analysis, as shown in Figure 1. Crystals of the triene formed in the monoclinic

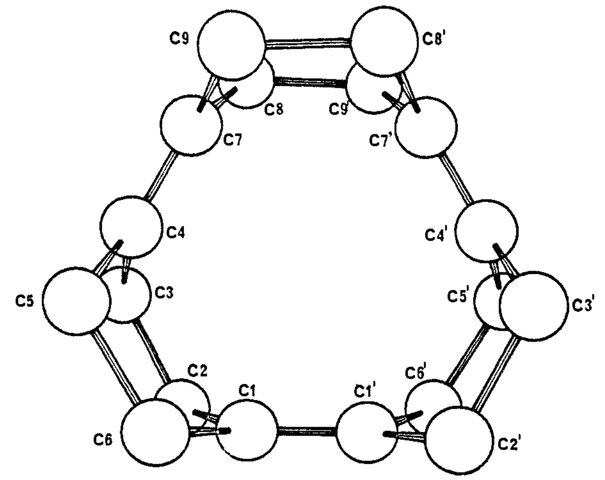


Figure 1. A computer-generated perspective drawing of the final X-ray model of triene **3**. Hydrogens are omitted for clarity, and there is a molecular twofold axis. The average unique bond distances are the following 1.342 (9), 1.509 (7), and 1.537 (8) Å. The double bond carbons are 0.14 Å out of the plane defined by the four attached carbon atoms.

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Table I. Interatomic Distances and Bond Angles for Triene 3

atoms	distance (Å)	atoms	distance (Å)
C1–C1′	1.342 (9)	C1–C4	2.602 (4)
C1–C2′	2.518 (3)	C1–C7	3.457 (5)
C1–C3′	3.503 (6)	C2–C3	1.537 (8)
C1–C4′	3.465 (4)	C2–C5	2.946 (6)
C1–C7′	3.925 (4)	C2–C6	2.478 (5)
C1–C2	1.509 (7)	C2–C6′	3.919 (5)
C1–C3	2.508 (6)		

bonds	angle (deg)
C1–C1′–C2′	124.6 (3)
C1–C2–C3	109.9 (3)
C2–C1–C6	110.2 (3)

Table II. Vertical Ionization Energies ($I_{v,j}$) and Calculated (MINDO/3) Orbital Energies (ϵ_j) of Triene 3

band	$I_{v,j}$	assignment	$-\epsilon_j$
1	7.9	$6a_1'(\pi)$	8.71 ($6a_1'$)
	8.1	$9e'(\pi)$	9.19 ($9e'$)
3	8.3		
4	9.5	$3a_1''(\sigma)$	9.34 ($3a_1''$)

space group $C2/c$ with a = 13.889 (1) Å, b = 7.9690 (7) Å, c = 13.137 (1) Å, and β = 112.19 (1)°. The molecule used a crystallographic twofold axis, and the asymmetric unit was C_9H_{12}. A phasing model was found routinely with MULTAN, and refinement in CRYSTALS converged to a conventional discrepancy index of 0.0607 for the observed data.[9] Table I gives the most important interatomic bond distances and angles.

As indicated in Figure 1, triene 3 has a threefold symmetry axis. The three six-membered rings are boat-like, and the double bond carbons are 0.14 Å out of the plane defined by the four attached carbons. This deformation produces a slight outward pucker of the double bond carbons, enhancing electron density on the exterior of the molecule. The C1–C4 distance between neighboring double bond carbons is 2.60 Å. Perpendiculars drawn from the midpoints of the three double bonds intersect on the threefold axis at a point 2.07 Å from each bond.

Photoelectron Spectroscopy of Triene 3. Our primary interest in synthesizing triene 3 was to examine the possibility that ppσ overlap of the six interior p lobes might lead to the stabilization of the molecule via trishomoaromaticity. Although other molecules with similar double bond arrangements have been prepared, including 1(Z),4(Z),7(Z)-cyclononatriene **15**, triquinacene **16**, and C_{16}-hexaquinacene **17**, none exhibit trishomoaromaticity if a ring-current criterion is used.[10] Molecular models indicate, however, that the three double bonds in triene 3 may be better aligned for overlap than in **15**, **16**, or **17**. Thus, in **15** and **16**, the double bonds have an out-of-plane cant that diminishes the effectiveness of orbital overlap,[11,12] whereas the double bonds in 3

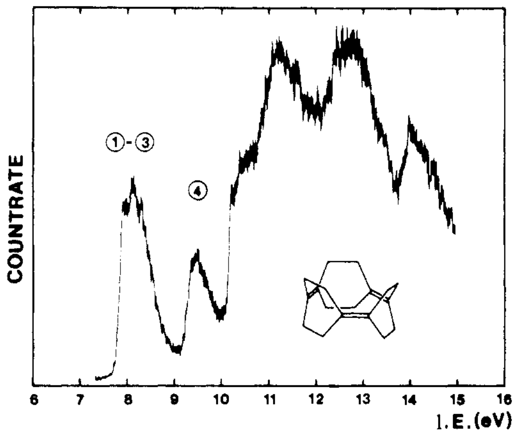


Figure 2. He I photoelectron spectrum of triene 3.

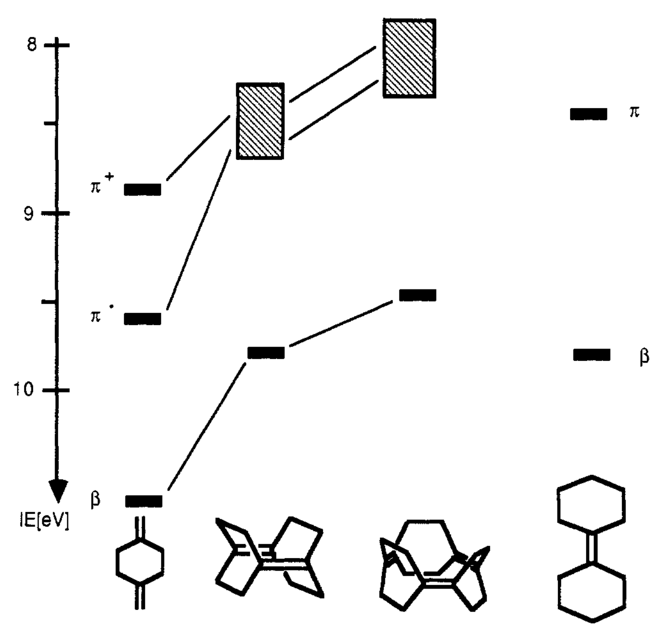
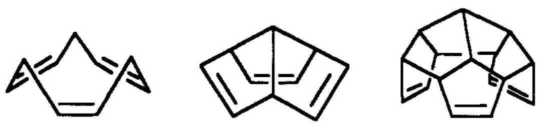


Figure 3. Comparison between the first bands in the photoelectron spectra of triene 3 and those of **18** and **19**.

lie in a common plane. In addition, the measured double bond distance in **17** is 2.85 Å,[10] whereas the distance in 3 is 2.60 Å.



15 16 17

Photoelectron (PE) spectroscopy is the technique most suited for probing potential interactions among π bonds.[13] Indeed, compounds **15**, **16**, and **17** have already been examined by He I PE spectroscopy, and separations for bands corresponding to ionization from e(π) and a_1(π) orbitals have been reported. The band split for **15** is 0.9 eV,[14] while values of 0.4 and 0.47 eV have been reported[10,15] for **16** and **17**, respectively. On the basis of the assumption that the measured vertical ionization energies ($I_{v,j}$) can be set equal to the negative value of the calculated orbital

(9) All crystallographic calculations were done on a PRIME 950 computer operated by the Cornell Chemistry Computing Facility. Principal programs used were: REDUCE and UNIQUE, data reduction programs by M. E. Leonowicz, Cornell University, 1978; MULTAN 78, a system of computer programs for the automatic solution of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculations including Patterson syntheses) written by P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1978; BLS78A, an anisotropic block diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; CRYSTALS, a crystallographic system written by D. J. Watkin and J. R. Carruthers, Chemical Crystallography Laboratory, University of Oxford, 1981; PLUTO78, a crystallographic illustration program by W. D. S. Motherwell, Cambridge Crystallographic Data Centre, 1978; and BOND, a program to calculate molecular parameters and prepare tables written by K. Hirotsu, Cornell University, 1978.

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energies ($-\epsilon_j$) (Koopmans' approximation[16]) photoelectron spectroscopy is the method of choice to probe the orbital interactions in **3**.

The PE spectrum of **3** is shown in Figure 2, and the first ionization energies are recorded in Table II. The spectrum shows a relatively broad band around 8.1 eV, well separated from a smaller one near 9.5 eV. The ratio of peak areas is 3:1.

To assign the spectrum, we proceed in two ways: (1) We used an empirical correlation with similar molecules, and (2) we compared the sequence of bands with the results of semiempirical MO calculations. Our empirical assignments are based on comparison with the PE spectra of 1,4-bis(methylene)cyclohexane (**18**), tricyclo[4.2.2.2^{2,5}]-1,5-dodecadiene (**2**), and bicyclohexylidene (**19**). The PE of all three molecules have been reported in the literature.[17-19]

We started our empirical assignment with the PE spectrum of **18**.[17] The two bands at 8.9 and 9.6 eV can be assigned to ionization from $7a_g(\pi^+)$ and $6b_u(\pi^-)$, respectively, assuming C_{2h} symmetry. The first ionization energies of **18** are shown on the left of Figure 3 and are correlated with the first PE bands of **2**.[18]

Although this correlation is not straightforward owing to strong conformational changes of the six-membered ring that alter the interaction pattern, the essential features can be seen from Figure 3. Further bridging of the ethylene units in **18** and adoption of a boat-like conformation will yield a smaller shift of the first band compared with the second one. The corresponding shifts toward higher energy of the first π MO (HOMO) of **18** can be explained by the inductive effect of the larger σ frame and consequent increased C–H hyperconjugation. The larger shift of the second π MO is caused by an additional through-bond interaction[20] with the C–C σ bonds of the bridges.

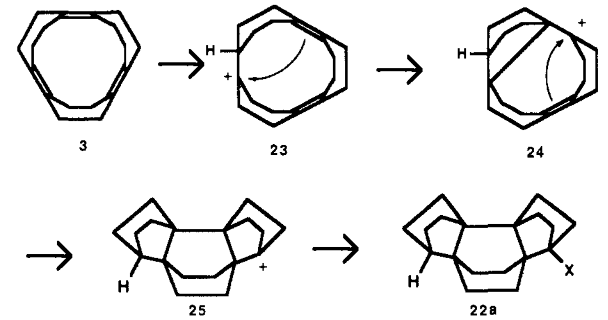
The PE spectrum of **2** is very similar to that of **3** with respect to the shapes and positions of the first two peaks. The main difference is the ratio of the areas below the peaks (2:1 for **2** and 3:1 for **3**). This suggests that the first peak should be assigned to ionization from the π fragments of both compounds. A comparison between the positions of the first two peaks in the PE spectra of **3** and **2** with that of **19**[19] shows a great similarity (Figure 3), which further corroborates the assignment.

The empirical assignment of the first PE bands in **3** is confirmed by semiempirical calculations. Using the MINDO/3 method,[21] we have computed the orbital energies of **3**, with the results shown in Table II. The calculations predict three close-lying π orbitals on top of the σ orbitals for **3**. The gap between π and σ orbitals is smaller than that found in experiment.

The assignment of the PE spectra of **3** given in Table II and Figure 2 reveals a relatively small split the between the π bands, indicating only a small interaction between the π fragments. This result can be understood by considering the distances between the termini of the π fragments (2.60 Å) and comparing them with those reported for **16** (2.53 Å)[12] and **17** (2.85 Å).[10] In the latter two compounds, the split between $e(\pi)$ and $a_1(\pi)$ is of the same order of magnitude as for **3**. The semiempirical calculations also reveal a similar π/σ interaction of **3**, **16**, and **17**.

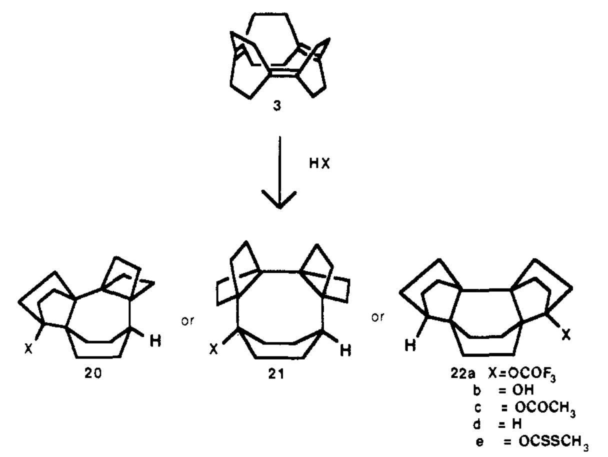
Chemistry of Triene 3. Since we expected triene **3** to show unusual reactivity for steric reasons, our initial chemical explorations centered on its reactions with electrophiles. In fact, **3** proved extremely reactive toward a variety of electrophiles, though in no case were simple 1,2-adducts formed. For example, treatment of **3** with trifluoroacetic acid in dichloromethane solution

Scheme II. Acid-Catalyzed Rearrangement Pathway for Triene 3



resulted in rapid disappearance of starting material and quantitative formation of a 1:1 trifluoroacetate adduct. Brief exposure to dilute aqueous NaOH gave the corresponding alcohol. Although the ^1H NMR spectrum of the adduct was complex and uniformative, the twelve-line ^{13}C NMR spectrum (δ 82.72, 48.10, 47.92, 47.14, 46.07, 40.53, 35.76, 32.01, 31.47, 29.98, 24.56, 22.65) indicated the presence of a symmetry plane and the absence of vinylic carbons. Thus, a transannular rearrangement appears to have occurred.

There are three structures, **20**, **21**, and **22**, that fit the ^{13}C NMR data for the trifluoroacetic acid adduct of triene **3**. Though all three might result from reasonable rearrangement pathways, structures **20** and **21** contain highly strained bicyclo[2.2.0]hexane ring systems, whereas **22** is undoubtedly much less strained.



In attempting to devise ways to distinguish among the three structures, it occurred to us that reduction of the hydroxyl group (**22b** → **22d**) would introduce an additional symmetry plane into both **21** and **22** but not into **20**. Carbon NMR could then be used either to rule out or to confirm structure **20**. Unfortunately, we were unable to effect the reduction. Attempted ionic reduction of alcohol **22b** by treatment with trifluoroacetic acid and triethylsilane[22] gave only recovered alcohol. Similarly, photolysis of the corresponding acetate **22c** in aqueous HMPA[23] yielded only recovered alcohol; reduction of acetate **22c** with lithium in ethylamine[24] gave only recovered alcohol; and treatment of the corresponding xanthate ester with tri-*n*-butyltin hydride[25] gave only alcohol. These results presumably reflect the instability of the potential bridgehead radical and/or cation intermediates in the various reactions.

Unable to obtain the positive evidence that would have been provided by reduction of the triene/trifluoroacetic acid adduct, we sought negative evidence instead. It is known[26] that bicy-

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clo[2.2.0]hexane ring systems are thermally unstable, undergoing ring opening at temperatures above 100 °C to yield 1,5-dienes. Bicyclo[2.2.0]hexane itself, for example, ring opens at 130 °C. The alcohol obtained from hydrolysis of the triene/trifluoroacetic acid adduct was pyrolyzed by dropping it slowly down a quartz tube heated to 500 °C but was recovered unchanged. Since it is unlikely that either **20** or **21** could survive such treatment, we assign structure **22** to the adduct.[27]

How does structure **22** arise? The most straightforward mechanistic pathway for the formation of **22** involves protonation of a double bond to yield cation **23**, followed by a first transannular cyclization giving cation **24**, a second transannular cyclization giving cation **25**, and quenching with trifluoroacetate anion (Scheme II).

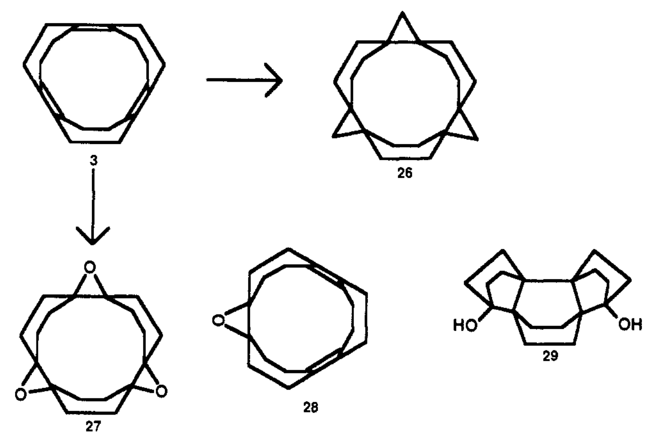
Other attempted electrophilic-addition reactions of triene **3** met with mixed success. Reaction of **3** with acetic acid in the presence of a catalytic amount of trifluoromethanesulfonic acid led rapidly and quantitatively to acetate **22c**. Reaction with bromine in CCl_4 and with HCl in ether, however, led to complex mixtures of products that could not be separated. Attempted hydroxylation by treatment of **3** with osmium tetraoxide was unsuccessful when no reaction occurred. This latter result was expected because the reaction would have had to occur by a sterically unfavorable concerted syn addition.

Our fundamental conclusion from the above results is that 1,2-addition to triene **3** is unfavorable, either when a cationic intermediate is involved so that rearrangements can occur or when an unfavorable geometric change is required so that steric strain is increased. Neither situation should obtain in the conversion of a double bond to a three-membered ring, however. Both epoxidation by peroxy acid and cyclopropanation by Simmons-Smith reaction take place without carbocation intermediates, and neither results in a drastic geometric change. Thus, both reactions might be expected to occur smoothly on triene **3**.

Both cyclopropanation and epoxidation of **3** do, in fact, take place easily. Though standard Simmons-Smith conditions using diiodomethane and zinc-copper couple led to variable results, reaction in the presence of excess diiodomethane and diethylzinc[28] gave triscyclopropane **26** in greater than 90% yield (^{13}C NMR δ 28.32, 28.02, 25.93). Similarly, reaction of triene **3** with excess *m*-chloroperoxybenzoic acid in dichloromethane gave trisepoxide **27** in quantitative yield. As might be expected, trisepoxide **27** showed remarkable stability towards acids because it has no obvious reaction pathways. Normal anti epoxide ring opening is precluded by the cyclic structure of **27**; syn ring opening is precluded both by mechanism and by the unfavorable geometry of the resultant product; and transannular rearrangement is precluded by the lack of double bonds. Thus, trisepoxide **27** was recovered unchanged after being stirred for 1 week in 12 M hydrochloric acid.

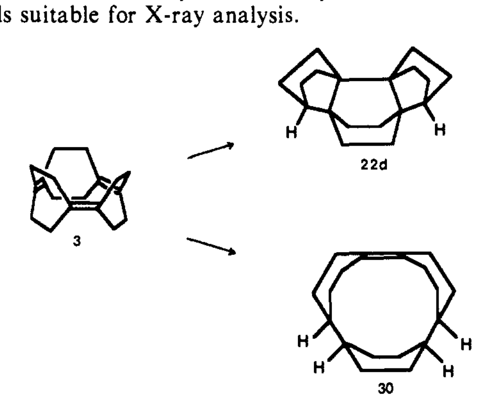
Careful reaction of triene **3** with 1 equiv of *m*-chloroperoxybenzoic acid successfully provided monoepoxide **28** in a surprising 69% yield. As expected, this monoepoxide proved sensitive to acid. Attempted hydrolysis by reaction with aqueous perchloric acid in tetrahydrofuran gave a complex mixture of products, but reaction with trifluoroacetic acid in dichloromethane solution gave a single product that could be easily saponified to yield a diol. The symmetry of the diol, unambiguously shown by its six-line ^{13}C NMR spectrum (δ 82.24, 47.56, 46.67, 35.64, 30.70, 22.18), was consistent with the expected rearrangement product **29**.

Our final experiments on triene **3** involved attempted hydrogenations and dehydrogenations. Treatment of **3** with sodium metal in hexamethylphosphoramide under conditions that are known[29] to reduce isolated double bonds gave a mixture of products from which a saturated hydrocarbon with symmetry corresponding to **22d** could be isolated (^{13}C NMR δ 47.68, 47.51, 41.22, 32.94,



30.18, 25.19). This compound is, of course, the same hydrocarbon we had earlier tried to prepare without success by reduction of the triene/trifluoroacetic acid adduct **22b**. Coincidentally, the same substance was formed by treatment with palladium-on-carbon in refluxing decalin.[30] Our thought in carrying out this latter reaction was that we might be able to effect dehydrogenation of the six ethylene bridges and form a fully unsaturated analogue of **3**. To our surprise, however, only the *hydrogenated* product **22d** was formed in a yield of 62%. This reduction presumably results from a disproportionation of the triene, although the disproportionation byproduct could not be isolated.

Catalytic hydrogenation of **3** was also attempted under a variety of reaction conditions. Though inert to reduction over platinum catalysts, even at high pressure, reaction with hydrogen at 50 psi of pressure over a rhodium on carbon catalyst led to uptake of 2 equiv of H_2 and formation of a tetrahydro product, presumably **30**, in 81% yield. No dihydro product could be detected if the reaction was stopped prematurely, and no hexahydro product was formed even under more forcing conditions. We consider the formation of **30** quite surprising in view of the high strain energy it must surely contain, but the product's symmetry (^{13}C NMR δ 129.02, 32.37, 31.06, 26.05, 25.75, 24.38) and the fact that it contains a symmetrical double bond are consistent with this structure. Unfortunately, we have as yet been unable to obtain crystals suitable for X-ray analysis.



Experimental Section

NMR spectra were recorded on Varian EM360, Jeol FX90Q, or Bruker WM-300 instruments. Mass spectra were recorded on an AEI-MS902 instrument. Melting points were determined on a Thomas-Hoover Uni-melt apparatus and are uncorrected. The phrase "worked up in the usual manner" refers to washing the reaction extract with saturated brine, drying the organic layer with anhydrous sodium sulfate, filtering the solution through a sintered glass filter, and concentrating the product by solvent removal at the rotary evaporator. Unless otherwise indicated, all reactions were conducted under an atmosphere of dry argon in glassware dried at 130 °C.

Photoelectron spectra were recorded on a Perkin-Elmer PS 18 photoelectron spectrometer with a He I_α lamp as the light source. Triene

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3 required heating to 110 °C to obtain its spectrum, which was calibrated with argon and xenon. A resolution of about 20 meV on the argon line was obtained.

Hydrazone 10. A solution of the monoacetal of 1,4-cyclohexanedione (**9**: 17.12 g, 93.0 mmol) and 1 drop of acetic acid dissolved in 50 mL of dichloromethane was added to a stirred mixture of diethylphosphorohydrazidate (17.49 g, 103.4 mmol) and sodium sulfate in 200 mL of dichloromethane. The reaction mixture was stirred mechanically overnight, filtered through Celite, and concentrated by solvent removal under reduced pressure to yield 32.79 g of crude hydrazone **10**. Recrystallization from *tert*-butyl methyl ether gave the pure product (28.43 g, 84.63 mmol, 91%): mp 88.5–90 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.27–1.4 (m, 6 H), 1.57 (br s, 4 H), 1.7–1.8 (m, 4 H), 2.2–2.4 (m, 4 H), 3.66 (br s, 4 H), 4.0–4.2 (m, 4 H), 8.28 (d, J = 25 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 154.83, 154.05, 100.30, 62.99, 62.76, 61.92, 33.32, 31.83, 30.99, 29.57, 21.34, 16.89, 15.80; IR (KBr) 3180, 2920, 1620, 1440, 1250 cm^{-1}; mass spectrum calcd for $C_{14}H_{27}N_2O_5P$ 334.1657, found 334.1651.

Bisazine 11. Sodium hydride (303 mg of 50% oil suspension, 6.31 mmol) was washed free of oil and suspended in 50 mL of dry THF. Hydrazone **10** (2.08 g, 6.25 mmol) was added as a solid over 10 min, and 1,4-cyclohexanedione (350 mg, 3.12 mmol) in 10 mL of THF was then added dropwise over 45 min. After the green-black mixture was stirred an additional hour at room temperature, it was diluted with 25 mL of 5% triethylamine in hexane and filtered though a pad of silica gel. The silica pad was washed three times with ethyl acetate–hexane–triethylamine (1:1:0.1), the filtrates were combined, toluene was added, and the solvent was removed under reduced pressure to yield bisazine **11** as a pale yellow solid that contained a mixture of E and Z isomers (1.19 g, 2.53 mmol, 81%): ^{1}H NMR ($CDCl_3$, 60 MHz) δ 1.5–2.1 (m, 16 H), 2.4–2.8 (m, 16 H), 3.6–4.0 (br s, 8 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 164.66, 164.30, 163.11, 100.42, 33.62, 32.97, 32.55, 31.35, 29.75, 26.71, 24.86, 23.67; IR (KBr) 2900, 1640, 1440, 1290 cm^{-1}; mass spectrum, calcd for $C_{26}H_{40}N_4O_4$ 472.3049, found 472.3036.

Bisthiadiazoline 12. Bisazine **11** (57 g, 120.8 mmol) was suspended in 2 L of dry acetonitrile and dissolved by warming with a heat gun. The homogeneous solution was then stirred rapidly overnight under an atmosphere of hydrogen sulfide (balloon) to yield a white precipitate. Filtration of the precipitate followed by washing with cold *tert*-butyl methyl ether gave 50.0 g (77%) of product.

The crude solid prepared above was added over 10 min to an ice-cold suspension of $CaCO_3$ (107 g) and lead tetraacetate (107 g, 240.8 mmol, 2.6 equiv) in 3 L of dichloromethane. After the mixture was stirred rapidly for 30 min, saturated sodium bicarbonate (1.0 L) was added, and stirring was continued an additional 20 min. The resulting two-phase mixture was filtered through Celite, the phases were separated, and the organic phase was washed with saturated sodium bicarbonate. The organic portion was dried ($MgSO_4$), filtered, and concentrated at the rotary evaporator to yield crude solid bisthiadiazoline **12** (50.56 g). Chromatography on silica gel (elution with 10% ethyl acetate in benzene) gave the pure product as a mixture of isomers (31.47 g, 63%): ^{13}C ($CDCl_3$, 22.5 MHz) δ 110.79, 110.55, 108.82, 107.63, 99.59, 61.91, 38.21, 37.31, 36.78, 31.83, 29.69; IR (KBr) 2910, 1550, 1440, 1260 cm^{-1}.

Diketone 6. Bisthiadiazoline **12** (29.9 g, 55.79 mmol) was dissolved in 4.0 L of dichloromethane, and 1.5 L of 37% aqueous HCl was added. After the mixture was stirred for 7 min, the phases were separated. The organic phase was washed with water and with saturated sodium bicarbonate and then dried. Filtration through Celite and solvent removal at the rotary evaporator yielded 20.95 g of crude product.

The crude product prepared above (20.95 g, 53.44 mmol) was suspended in 2.2 L of toluene and refluxed for 2.5 h to extrude nitrogen. Triethyl phosphite (84.8 g, 510.4 mmol) was added and the mixture was refluxed overnight. After the mixture was cooled to room temperature, solvent was removed under reduced pressure, first at the aspirator and then at high vacuum. Crystallization of the semisolid residue from *tert*-butyl methyl ether gave pure diketone **6** (10.57 g, 38.82 mmol, 73%): mp 152–154 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.54, (t, J = 6.2 Hz, 8 H), 2.38 (t, J = 6.2 Hz, 8 H), 2.30 (s, 8 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 212.57, 131.29, 124.61, 40.29, 28.79, 26.49; IR (KBr) 2820, 2880, 1700 cm^{-1}; mass spectrum, calcd for $C_{18}H_{24}O_2$ 272.1776, found 272.1763. Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found C, 79.36; H, 8.98.

Tetracyclo[8.2.2.2^{2,5}.2^{6,9}]-1,5,9-octadecatriene (3). Titanium trichloride (17.47 g, 113.15 mmol, 30 equiv) and zinc–copper[31] (19.0 g, 290.5 mmol) were transferred under argon atmosphere to a 2-L round-bottomed flask. Dry dimethoxyethane (1.0 L) was then added, and the mixture was then refluxed for 5 h to form the active titanium coupling reagent. After the reaction was cooled to 68 °C, diketone **6** (1.0 g 3.68 mmol) in 200 mL of dimethoxyethane was added over 45 h via syringe pump, followed by additional stirring at 68 °C for 2 h. The reaction mixture was then cooled to room temperature, diluted with benzene (600 mL), and filtered through a pad of Florisil. The black titanium salts were washed four times with 1:1 benzene–ethyl acetate, the organic layers were combined, and solvent was removed under reduced pressure to yield 798 mg of crude white solid. Sublimation of the crude solid at 100 °C under 0.05 mm of pressure gave a white powder that was recrystallized from ethyl acetate to provide pure triene **3** (214 mg, 24%): mp 259–259.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.46 (m, 12 H), 2.01 (m, 12 H) (AA′BB′ symmetrical pattern); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 129.86, 28.43; mass spectrum, m/z 240 (100%, M$^+$). Anal. Calcd for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 90.09; H, 9.82.

Trifluoroacetate 22a. Trifluoroacetic acid (0.1 mL) was added to a solution of triene **3** (10 mg, 0.042 mmol) in 10 mL of dichloromethane, and the solution was allowed to sit for 1 h at room temperature. Solvent was then removed under reduced pressure to yield trifluoroacetate **22a** (14.5 mg, 98%) as the sole product: mp 107–109 °C; ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 163.40, 108.17, 93.03, 48.51, 48.21, 47.61, 43.98; IR (KBr) 2970, 2840, 1765 cm^{-1}; mass spectrum, calcd for $C_{20}H_{25}O_2F_3$ 354.1806, found 354.1807.

Alcohol 22b. Trifluoroacetate **22a** (13.8 mg, 0.039 mmol) was dissolved in 11 mL of THF, and 1 mL of 2% aqueous NaOH was added. After the mixture was stirred for 30 min, the reaction was worked up in the usual way to give crude alcohol **22b**. Chromatography on silica gel (elution with 20% ethyl acetate in hexane) gave the pure product (7.0 mg, 70%): ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 82.72, 48.10, 47.92, 47.14, 46.06, 40.53, 35.76, 32.01, 31.47, 29.98, 24.56, 22.65; mass spectrum, m/z 258 (100%, M$^+$).

Triscyclopropane 26. Triene **3** (25 mg, 0.104 mmol) was dissolved in 19 mL of dry benzene, and diethylzinc (1.6 mL of a 25% solution in toluene, 4.0 mmol) was added. The solution was warmed to 60 °C and diiodomethane (250 μL, 3.1 mmol) in 1 mL of benzene was added over 3 h via syringe pump. After the mixture was stirred an additional h at 60 °C, the reaction was cooled to room temperature and 1 mL of water was cautiously added. The reaction was then acidified with dilute HCl and worked up in the usual way to yield crude triscyclopropane **26** (35 mg). Chromatography on silica gel (elution with pentane) gave the pure product (26.8 mg, 91%): mp 193–193.5 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) AA′BB′ symmetrical pattern at δ 1.3–1.5 (m, 12 H) and 1.75–2.0 (m, 12 H), –0.05 (s, 6 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 28.32, 28.02, 25.93; mass spectrum, m/z 282 (15%, M$^+$).

Trisepoxide 27. Triene **3** (3.2 mg, 0.013 mmol) was dissolved in 3 mL of dichloromethane, and *m*-chloroperoxybenzoic acid (15 mg of 80% purity, 0.07 mmol) was added all at once. After the mixture was stirred 30 min, 10 drops of 1-hexene were added to destroy excess oxidant, and stirring was continued an additional 30 min. Dilution of the reaction with dichloromethane, washing with saturated sodium carbonate solution, and workup in the usual manner gave the pure product **27** (3.7 mg, 100%): mp 258 °C dec; ^{1}H NMR ($CDCl_3$, 300 MHz), AA′BB′ symmetrical pattern at δ 1.68 (m, 12 H) and 2.18 (m, 12 H); mass spectrum, m/z 288 (30%, M$^+$).

Monoepoxide 28. *m*-Chloroperoxybenzoic acid (21.6 mg, 0.125 mmol) was added to a solution of triene **3** (30.0 mg, 0.125 mmol) in 20 mL of dichloromethane at –10 °C. After the solution was stirred for 20 min at –10 °C, the solvent was removed under reduced pressure, and the crude residue was chromatographed on silica gel. Elution with 4% ethyl acetate in hexane gave 4.5 mg of recovered triene **3** and 19 mg (69% yield, 59% conversion) of pure monoepoxide **28**: mp 192–193 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.55–1.7 (m, 4 H), 1.97–2.2 (m, 12 H), 2.44–2.63 (m, 8 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 129.98, 128.90, 67.47, 28.43, 24.98; IR (KBr) 2930, 2860, 2810, 1480, 1150 cm^{-1}; mass spectrum, calcd for $C_{18}H_{24}O$ 256.1827, found 256.1830.

Diol 29. Trifluoroacetic acid (0.5 mL) was added to an ice-cold solution of epoxide **28** (22.8 mg, 0.089 mmol) in 20 mL of dichloromethane, and the solution was stirred for 5 min. Removal of the solvent under reduced pressure gave a white solid that was dissolved in 10 mL of methanol and treated with 4 mL of methanol–water–NaOH (90:5:5). After the mixture was studied for 15 min at 0 °C, solvent was removed at the rotary evaporator, and the residue was partitioned between dichloromethane and water. Workup of the organic portion in the usual way gave crude diol **29**. Chromatography on silica gel (elution with 1:1 ethyl acetate/hexane) provided pure product (18.2 mg, 75%): mp 133–134.5 °C; ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 82.24, 47.56, 46.67, 35.64, 30.70, 22.18; IR (KBr) 3200 (br), 1510, 1300, 1180 cm^{-1}; mass spectrum, calcd for $C_{18}H_{26}O_2$ 274.1933, found 274.1933.

Hexacycloalkane 22d. Triene **3** (10.0 mg, 0.042 mmol) and 5% Pd on activated carbon (10.0 mg) were suspended in 4 mL of decalin, and the reaction mixture was refluxed under argon for 22 h. Filtration and

(31) Prepared by the method of Krepski. See ref 8 in: McMurry, J. E.; Kees, K. L. *J. Org. Chem.* **1977**, *42*, 2655.

solvent removal under high vacuum gave a crude product that was chromatographed on silica gel (elution with pentane) to provide hydrocarbon **22d** (6.4 mg, 62%): mp 116–117 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.11–1.32 (m, 11 H), 1.54–1.91 (m, 15 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 47.68, 47.51, 41.22, 32.94, 30.18, 25.19; mass spectrum, m/z 242 (91%, M^+).

Monoolefin 30. Triene **3** (25 mg, 0.10 mmol) was dissolved in 10 mL of hexane, and 5% Rh on carbon (20 mg) was added. After degassing, the solution was shaken under an atmosphere of hydrogen gas (48 psi) for 60 h at room temperature. Filtration and removal of solvent yielded monoolefin **30** as the sole product (19.6 mg, 81%): mp 162–163 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.3–2.2 (m, 24 H), 2.3–2.56 (m, 4 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 129.02, 32.37, 31.06, 26.05, 25.75, 24.38; mass spectrum, m/z 244 (100%, M^+).

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Registry No. 3, 91266-48-7; **6**, 91266-53-4; (*cis*)-**6** (thiirane), 101713-72-8; (*trans*)-**6** (thiirane), 101713-73-9; **9**, 80427-20-9; **10**, 91266-49-8; (*E*)-**11**, 101713-64-8; (*Z*)-**11**, 101713-65-9; (*cis*)-**12**, 101713-68-2; (*trans*)-**12**, 101713-69-3; (*cis*)-**12** (hydrazine), 101713-66-0; (*trans*)-**12** (hydrazine), 101713-67-1; (*cis*)-**12** (deprotected), 101713-70-6; (*trans*)-**12** (deprotected), 101713-71-7; **13**, 91266-54-5; **14**, 6051-37-2; **22a**, 101713-74-0; **22b**, 101713-75-1; **22c**, 101713-76-2; **22d**, 101713-77-3; **22e**, 101713-78-4; **26**, 101713-79-5; **27**, 101713-80-8; **28**, 101713-81-9; **29**, 101713-82-0; **29** (trifluoroacetate), 101759-50-6; **30**, 101713-83-1; $H_2NNHPO(OEt)_2$, 56183-69-8; 1,4-cyclohexanedione, 637-88-7.

Solid-State ^{2}H NMR, ^{57}Fe Mössbauer, and X-ray Structural Characteristics of μ_3-Oxo-Bridged Mixed-Valence $[Fe_3O(O_2CCH_3)_6(4\text{-Me-py})_3](C_6H_6)$: Dynamics of the Benzene Solvate Molecules Influencing Intramolecular Electron Transfer

Scott E. Woehler,[1] R. J. Wittebort,*[1] Seung M. Oh,[2] David N. Hendrickson,*[2] Daryl Inniss,[3] and Charles E. Strouse*[3]

Contribution from the Department of Chemistry, University of Louisville, Louisville, Kentucky 40292, the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801, and the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. *Received October 28, 1985*

Abstract: Intramolecular electron transfer is investigated in the mixed-valence complex $[Fe_3O(O_2CCH_3)_6(4\text{-Me-py})_3](C_6H_6)$, where 4-Me-py is 4-methylpyridine. Rotational motion of the benzene solvate molecule and the possible influence of this motion on the rate of intramolecular electron transfer are studied crystallographically and spectroscopically. The compound crystallizes in the rhombohedral space group $R32$; $a = b = 18.552$ (3) Å, $c = 10.556$ (2) Å at 133 K with $Z = 3$. The final discrepancy factors are $R = 0.048$ and $R_w = 0.061$ for 1209 reflections with $I > 3\sigma(I)$. Complex molecules and disordered benzene solvate molecules are stacked in alternate sites of 32 symmetry along the 3-fold c axis. The unit cell contains three such stacks related by a 3_1 axis. The 4-Me-py ligands are nearly coplanar with the Fe_3O moiety. The 3_1 axis passes through the three nearly parallel 4-Me-py ligands of three adjacent stacks. The interligand separation, $c/3 = 3.51$ Å, along the 3_1 axes probably controls the size of the solvate cavity along the 3-fold axis. Electron density maps indicate a preferred orientation for the benzene solvate molecule with its 6-fold axis perpendicular to both the crystallographic 3-fold and 2-fold axes. The large thermal parameter observed for the solvate molecule is consistent with a dynamic disorder of this group. Two doublets of area ratio 2:1 (Fe^{III}:Fe^{II}) are present in the Mössbauer spectrum at temperatures approaching liquid helium. As the sample temperature is increased above ~60 K, the spectrum changes to eventually become a single average-valence doublet at temperatures above ~200 K. The complex $[Fe_3O(O_2CCH_3)_6(4\text{-Me-py})_3](C_6D_6)$, in which perdeuteriobenzene is the solvate molecule, gives high-resolution ^{2}H NMR spectra. Spectra are readily obtained from three sample types: random powders, magnetically oriented microcrystals, and single crystals. The spectral properties are determined both by the motionally averaged ^{2}H quadrupolar coupling and by dipolar interactions of the deuterons with the unpaired electrons of the neighboring trinuclear complexes. These two types of interactions are readily separated in the ^{2}H NMR experiment. Single-crystal ^{2}H NMR data were obtained at room temperature by rotating a ~1 × 1 × 1 mm crystal about three mutually orthogonal axes. Temperature studies were also carried out for powdered and magnetically oriented microcrystalline samples in the range of ~150–293 K. From the orientation and magnitude of the residual ^{2}H quadrupolar coupling, it was concluded that the benzene solvate molecules are not only ring rotating about their C_6 axes, but they are also rotating about the C_3 stacking axes. An appreciable through-space dipolar interaction of the magnetic dipole of the deuterons with the magnetic dipoles of the nearby paramagnetic Fe_3O complexes is present.

The general goal in the study of mixed-valence transition-metal complexes has been to understand what factors determine the rate of electron transfer between well-separated metal ions through variation of the bridge between the metal centers.[4] It is frequently implicitly assumed[5] for a symmetric binuclear mixed-valence complex that the electronic coupling between the two metal ions

(1) University of Louisville.
(2) University of Illinois.
(3) University of California.

(4) For recent reviews see: (a) Day, P. *Intl. Rev. Phys. Chem.* **1981**, *1*, 149. (b) *Mixed-Valence Compounds, Theory and Applications in Chemistry, Physics, Geology and Biology*; Brown, D. B., Ed.; Reidel: Boston, 1980. (c) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1–73. (d) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107–129.

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