also been reported to yield rearranged allylic bromides and dienes.

Conclusions

1. TIBE reacts with Br_2 instantly to form a charge-transfer complex that ultimately evolves into a double bond shifted allylic bromide. The reaction with Br_2 is slow enough that information about the CTC and its formation constant can be obtained. The CTC formation constant is shown to have a small sensitivity to the nature of the solvent: K_f(solvent), 9.71 M^{-1} (CH_2ClCH_2Cl), $\leq$2.5 M^{-1} (methanol), 1.72 M^{-1} (acetic acid). Also, from the K_f values at 25 °C for cyclohexene, Ad=Ad, and TIBE in CH_2ClCH_2Cl of 0.47, 289, and 9.71 M^{-1}, respectively, it can be concluded that there are sizable structural effects on the CTC formation constants.

2. Kinetic studies of the reaction of **2**-H8 and **2**-D8 with Br_2 in acetic acid, 25 °C, gives evidence of a large kinetic isotope effect of 2.3 (0.1). This is too large for any β secondary KIE on a process where the rate limiting step is formation of a bromonium ion. The observed KIE is more consistent with a primary effect (superimposed on a secondary α effect of the remaining CL) in which a CL bond is breaking in a rate limiting or partially rate limiting step. Added acetate accelerates the reaction, not as a general base, but rather as a normal salt.

3. The best explanation for the KIE attributes the effect to deprotonation of the bromonium ion. That the KIE of 2.3 is at the low end of the values expected for a primary effect (2-7) is possibly because the TS for the ion decomposition is early, or that the isotope sensitive TS is only partially rate limiting because that barrier is similar in energy to the one that leads from the ion back to the CTC. In either case, the observation of the KIE requires that all steps preceding the rate limiting one(s) must have lower activation energies, which would suggest that the ionic intermediates (bromonium ion) must be reversibly formed.

4. Specially engineered olefins such as Ad=Ad or TIBE allow one to probe the reversible nature of bromonium ion formation. This results from raising the barriers for the product-forming steps to prevent production formation (as in the case of Ad=Ad) or deflecting the course of the reaction from addition into double bond rearranged substituted products as in the case of TIBE. In the absence of special features, the partitioning of a given bromonium ion between reversal and product formation is difficult to evaluate, but it is generally controlled by the relative barrier heights. One can envision a spectrum of situations ranging from exclusive ion reversal (Ad=Ad) to a progressively irreversible ion formation if the product-forming barrier is substantially lower than the reverse barrier. These relative barrier heights are expected to be sensitive functions of the structure, solvent, and nature of the ionic intermediates with respect to intimate ion pairs or solvent-separated ions. We do not claim bromonium ion reversal to be extant in all cases. However, what we have shown here, and in earlier reports,[2] is that the bromonium ions of TIBE and Ad=Ad (produced during bromination of the olefins in HOAc and DCE, respectively) and those of *cis*-stilbene, cyclohexene, and cyclopentene (formed solvolytically in DCE or HOAc) can reverse in accordance with the mechanism given in eq 1. This leaves open the possibility that ion reversal may be more prevalent than has been generally considered.

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Cyclopentannulation Reactions with Organoiron Reagents. Facile Construction of Functionalized Hydroazulenes

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Abstract: Troponeiron tricarbonyl, 2-methyltroponeiron tricarbonyl, and 4-methyltroponeiron tricarbonyl are converted to fluxional tropyliumiron tricarbonyl salts by treatment with either trimethylsilyl or di-*n*-butylboron triflate. These pentadienyliron cations react with (η^1-allyl)-, (η^1-propargyl)-, and (η^1-allenyl)Fp complexes [Fp = $C_5H_5Fe(CO)_2$] to give ketohydroazulene cycloadducts derived, in each reaction, from a single tautomeric tropylium cation. The further reaction of two such cycloadducts **14** and **22b** with lithium dimethyl cuprate gave tricyclic ketones **25a** and **b**, through a sequence depicted as involving initial formation of an anionic acyliron complex, followed by migratory insertion and an intramolecular aldol condensation.

Although no single cycloaddition reaction, comparable to the Diels-Alder reaction in its breadth of synthetic power, is available for the construction of five-membered carbocycles, a number of [3 + 2] cycloaddition reactions of more limited scope have been devised. These include reactions in which the three-carbon unit is variously an allenylsilane,[1] a cyclopropylphosphonium salt,[2] a (bromoacetylmethylene)triphenylphosphorane,[3] a cyclopropenone ketal,[4] an α,α'-dibromoketone,[5] a 1,3-diyl diradical,[6] a trimethylenemethane-palladium complex,[7] an acryloyl chloride,[8] or 3-iodo-2-[(trimethylsilyl)methyl]propene.[9]

Some time ago we showed that the (η^1-allyl)Fe complex **1** (Fp = $CpFe(CO)_2$) and the congeneric (η^1-allenyl)-, (η^1-propargyl)-, and (cyclopropyl)Fp complexes react as 1,3-dipole equivalents with either carbon or heteroatomic electrophiles in a highly regio- and stereospecific, two-step cycloaddition process to give five-membered carbocyclic and heterocyclic rings.[10]

(1) Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935. Danheiser, R. L.; Becker, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 389.
(2) Fuchs, P. L. *J. Am. Chem. Soc.* **1974**, *96*, 1607. Marino, J. P.; Landich, R. C. *Tetrahedron* **1975**, 4531.
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(7) Trost, B. M. *Angew. Chem.* **1986**, *25*, 1 and references therein.
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(9) Molander, G. A.; Shubert, D. C. *J. Am. Chem. Soc.* **1986**, *108*, 4683.
(10) Rosenblum, M. *J. Organomet. Chem.* **1986**, *300*, 191 and references therein.

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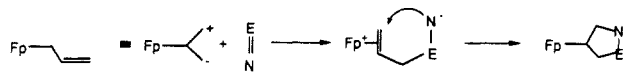
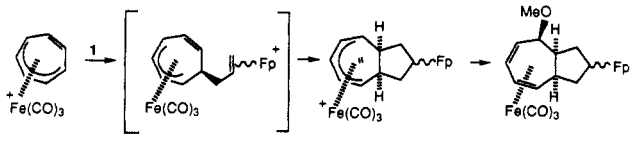


1

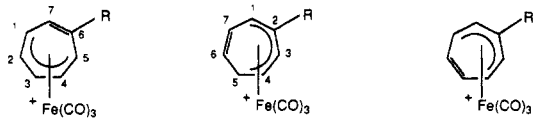
When the initiating electrophile is a tropyliumiron tricarbonyl, which can itself function as a 1,2-dipole equivalent, these [3 + 2] cycloaddition reactions provide a facile synthesis of diiron hydroazulene complexes, which may be demetalated or further functionalized.[11] This is illustrated for **1**.

An interest in extending this chemistry to sesquiterpene synthesis led us to examine the introduction of oxygen at C-4 in the hydroazulene skeleton of **2** as a possible route to guaiazulenes. Although cation **2** had been observed to give the methoxyl complex **3** on treatment with methanol in the presence of K_2CO_3, attempts to introduce hydroxy at this position led instead to highly polar reduction products, which could not be characterized. Alternatively, attempts to effect demetalation of **3** with TMS iodide resulted in regeneration of **2**.



2 3

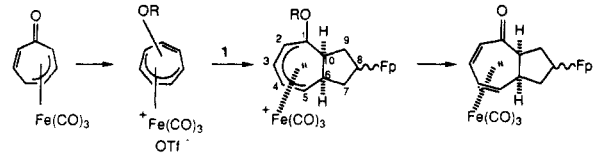
We turned therefore to an examination of the reactions of oxygen-substituted tropyliumiron tricarbonyl cations with Fp-activated 1,3-dipoles.[12] Such an approach introduces the potential problem of regioselectivity in the cycloaddition reactions, since the tropyliumiron tricarbonyl cation is known to be a fluxional system,[13] and a number of alkyl- and phenyl-substituted tropyliumiron tricarbonyl cations have been shown to exist as mixtures of isomers **4**, **5**, and lesser amounts of **6** in equilibrium at low temperature.[14] Nevertheless, the distribution of such isomers for oxygen-substituted tropylium ions was not known, and a kinetic discrimination in condensation reactions with organometallic nucleophiles such as (η^1-allyl)Fp could not be discounted.



4 5 6

R = Me, c-C_3H_5, i-C_3H_7, Ph

Initial attempts to alkylate troponeiron tricarbonyl with either trimethyl- or triethyloxonium tetrafluoroborate led to insoluble polymeric products apparently derived from the condensation of troponeiron tricarbonyl with the alkylated complex. However, trimethylsilyl or di-*n*-butylboron triflate was found to convert troponeiron tricarbonyl to the salt **7**, and this on treatment with **1** gave the cycloadduct **8**, as a mixture of C-8 epimers. Brief exposure of this salt to aqueous sodium bicarbonate yielded the neutral diiron complex **9** in 59% overall yield. The structural assignment for **9** is supported by ^1H and ^{13}C NMR spectra which show proton resonances for two protons each, between δ 5.2–5.8 and δ 2.4–2.6, as well as four methine carbon signals, two each in the range of δ 85–95 and δ 40–60, characteristic of a dieneiron tricarbonyl structure.[15] The infrared spectrum of the product exhibited both neutral metal carbonyl absorptions as well as a ketonic carbonyl absorption at 1631 cm^{-1}, indicative of the conjugated dienoneiron tricarbonyl structure.[14]

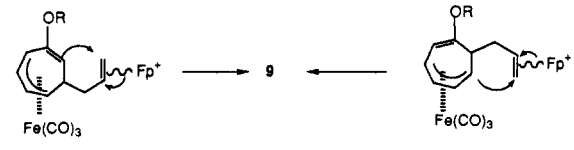


7 8 9

R = TMS, n-Bu_2B

The formation of **9** as a mixture of diastereomers, epimeric at C-8, is a consequence of nonstereoselective enantiofacial approach of the Fp(η^1-allyl) to the complexed tropylium ion in the initial step,[16b] while the cis ring fusion of the cyclopentane ring trans to the $Fe(CO)_3$ function finds ample precedent in the stereochemistry of the cycloaddition reactions of (η^1-allyl)Fp complexes and their congeners[16] and in the stereochemistry of nucleophile addition to pentadienyliron tricarbonyl cations.[17]

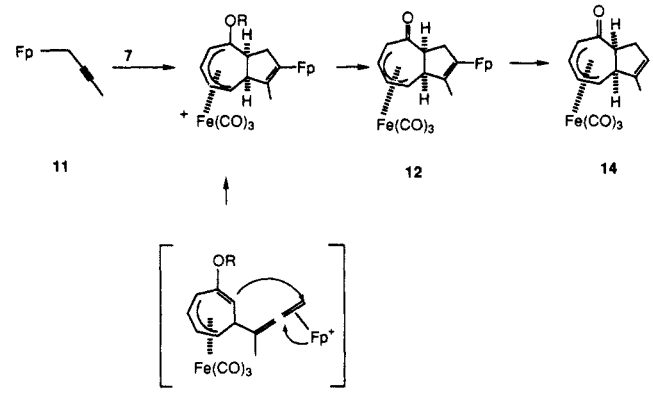
As has been observed in the condensation of tropyliumiron tricarbonyl with (η^1-allyl)Fe (**1**),[11] the reaction of **1** with **7** also occurs stepwise. The first step is apparently rapid at −78 °C, while the second requires refluxing in methylene chloride solution for 3 h for completion. The intermediate cation, detectable by its infrared spectrum, may be formulated as either **10a** or **10b**, with each derived from addition of **1** to the terminal carbon center of the complexed pentadienyl ligand[17] of **7**, that is to C-1 or C-5 of **4** or to C-1 of **5** (R = OTMS).



10a 10b

R = TMS, n-Bu_2B

In order to discriminate between these reaction paths, the condensation of (η^1-2-butynyl)Fp (**11**) with cation **7** was examined. When this reaction was carried out, by activating troponeiron tricarbonyl with either trimethylsilyl triflate or di-*n*-butylboryl triflate, a single neutral condensation product was obtained in 91% yield, after treatment of the initial cycloadduct with ethanolic potassium carbonate. Proton and ^{13}C NMR spectra of the product revealed resonances typical of the dienoneiron chromophore present in **9**. The addition of $Eu(fod)_3$ to these solutions resulted in methylene proton chemical shifts of 4–5 ppm, compared with methyl proton shifts of less than 1 ppm. Accordingly, the condensation product is assigned structure **12**. Its formation is best depicted as proceeding through addition of **11** to the least hindered terminal carbonyl center (C-1) of the pentadienyl ligand in tautomer **4** (R = OTMS) to give intermediate **13**.



11 12 14

13

As with **2**,[11] the Fp function in **12** may be selectively removed by exposure to 1% HCl at room temperature to give **14**. In order

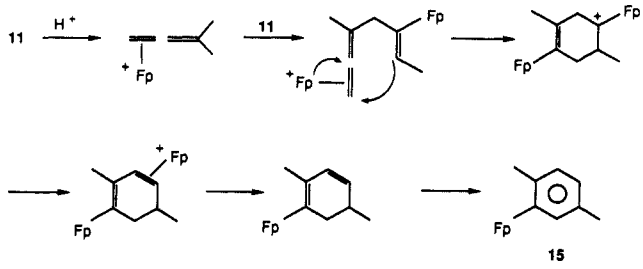
(11) Genco, N.; Marten, D.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1976**, *98*, 848. A number of cycloadditions of troponeiron tricarbonyl have also been reported. Howell, J. A. S.; Squibb, A. D.; Goldschmidt, Z.; Gottlieb, H. E.; Almadhoun, A.; Goldberg, I. *J. Am. Chem. Soc.* **1990**, *9*, 80 and references therein.

(12) For a preliminary account of this work, see: Watkins, J. C.; Rosenblum, M. *Tetrahedron Lett.* **1984**, *25*, 2097. Watkins, J. C.; Rosenblum, M. *Tetrahedron Lett.* **1985**, *26*, 3531.

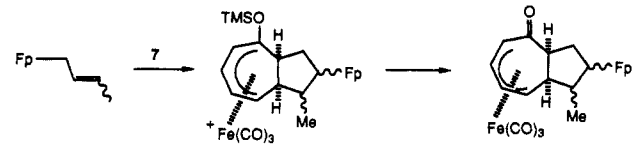
(13) Mahler, J. E.; Jones, D. A. K.; Pettit, R. *J. Am. Chem. Soc.* **1964**, *86*, 3589. Whitesides, T. H.; Budnik, R. A. *J. Chem. Soc., Chem. Commun.* **1971**, 1514. Whitesides, T. H.; Budnik, R. A. *Inorg. Chem.* **1976**, *15*, 874.

(14) Lewis, C. P.; Kitching, W.; Eisenstadt, A.; Brookhart, M. *J. Am. Chem. Soc.* **1979**, *101*, 4896.

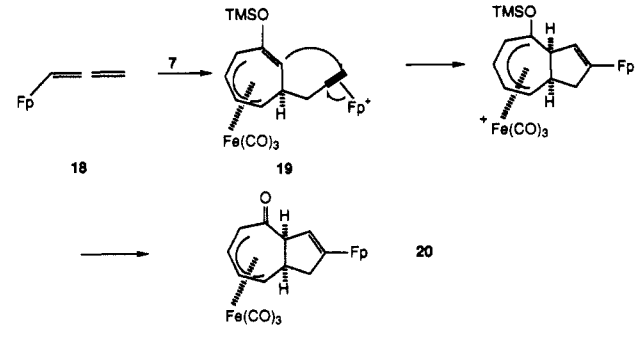
to achieve a high yield of **12** it was found necessary to use a four molar excess of the butynyl complex **11**, since in the presence of a trace of acid, which is difficult to exclude even in freshly distilled trimethylsilyl triflate or di-*n*-butyl triflate, **11** is rapidly transformed to the metalated *p*-xylene **15**. A plausible mechanism for the formation of **15** is outlined below.[18]



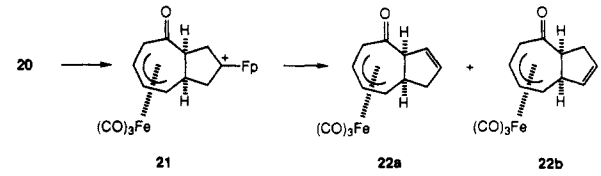
The condensation of **7** (R = Bu_2B) with an *E,Z* mixture of (2-butenyl)Fp (**16**), followed by mild base hydrolysis of the product gave the cycloadduct **17** as a mixture of cis and trans isomers.



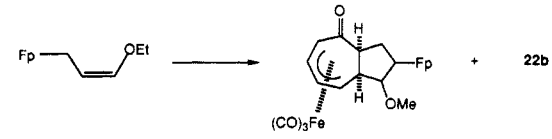
The use of the readily available (η^1-allenyl)Fp complex **18**,[16,19] in a reaction with **7** (R = Bu_2BOTf), provides a means of introducing unsaturation into the five-membered ring at C-8,9. The single product, obtained in high yield after mild base hydrolysis of the primary cycloadduct, is assigned structure **20** on the basis of a ^{13}C NMR shift experiment which shows a downfield shift of the vinyl CH carbon of 2.24 ppm in the presence of 20 mol % of Eu(fod)$_3$ compared with a shift of less than 1 ppm for the methylene carbon atom. As in the formation of **12**, the structure of this condensation product restricts the reaction path to one involving reaction of **18** with tautomer **4**, at C-1 to give intermediate **19**.



Demetalation of **20** with dilute HCl gave a 2:1 mixture of **22a** and **22b**, which could not be separated chromatographically. These isomers are not equilibrated under the conditions of their formation, and it therefore seems likely that demetalation proceeds through the intermediate cationic carbene complex **21**, followed by prototopic shift and loss of Fp cation.



Compound **22b**, free of **22a**, can be conveniently obtained from a cycloaddition employing (η^1-*cis*-1-ethoxylallyl)Fp (**23**) which is readily available from Fp(η^2-3-ethoxypropene)BF_4.[20] The intermediate keto ether **24** is a minor product of this reaction and is readily converted to **22b** by mild acid treatment.



Attempts to introduce substituents at C-5 in the hydroazulene complexes **8** (R = TMS, Me) by the addition of lithium dimethyl cuprate, dimethylcadmium, or lithium methyl cyanocuprate, led to ether cleavage and the regeneration of ketone **9**. The cleavage reaction could be suppressed by using the ethyl ether complex **8** (R = Et), which was prepared from **9** by treatment with triethyloxonium tetrafluoroborate, but only highly polar uncharacterizable products were obtained with both stabilized and unstabilized nucleophiles.

By contrast lithium dimethyl cuprate added readily to the uncharged dienoneiron complexes **22b** to give a single product in high yield. The IR spectrum of the product showed the loss of the iron tricarbonyl group and the presence of both a saturated carbonyl group (1700 cm^{-1}) as well as an alcohol function (3570 cm^{-1}). A proton NMR spectrum of the product revealed the presence of four vinyl protons between δ 5.66 and 6.13 and a methyl singlet resonance at δ 1.49. The ^{13}C NMR spectrum of the product confirmed the presence of four CH vinyl centers as well as a carbonyl and a methyl group and showed that two new carbon centers had been incorporated into the bicyclodecane framework. Structure **25a**, having a carbon skeleton closely related to that found in β-patchoulene,[21] is assigned to this product. Selective proton decoupling experiments further supported the assigned structure and allowed the stereochemistry of the hydroxyethylidene bridge relative to the hydrogens at C-6,10 to be made. Thus, the coupling constant for $J_{5,6}$ was determined to be 4.25 Hz, a value close to that of 4.2 Hz calculated for an MM-2 minimized structure in which the bridge is cis to the protons at C-6,10.[22] By contrast, this coupling constant for the trans isomer is calculated to be 2.2 Hz. The further assignment of the methyl substituent as anti to the C-3,4 olefinic bond is supported by the observation that hydrogenation of **25a** gives a tetrahydro compound in which the methyl proton resonance is shifted upfield slightly from δ 1.49 to 1.35 rather than downfield as would be anticipated for the epimeric structure.

A similar transformation of the uncharged iron carbonyl complex **12** by treatment with lithium dimethyl cuprate gave the tricyclic ketone **25b** in high yield.

A mechanism which accounts for these transformations is summarized below. Although attack of stabilized carbanions on 1,3-dieneiron tricarbonyl complexes has been observed to occur kinetically on the coordinated ligand at C-2,[23] simple alkyl and aryl lithio reagents as well as Grignards appear to react prefer-

(15) Churchill, M. *Prog. Inorg. Chem.* **1976**, *20*, 299. Brookhart, M.; Koszalka, G. W.; Nelson, G. O.; Scholes, G.; Watson, R. A. *J. Am. Chem. Soc.* **1976**, *98*, 8155.

(16) (a) Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495. (b) Bucheister, A.; Klemarczyk, P.; Rosenblum, M. *Organometallics* **1982**, *1*, 1679.

(17) Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463. Pearson, A. J.; Kole, S. L.; Chen, B. *J. Am. Chem. Soc.* **1983**, *105*, 4483. Pearson, A. J.; Yoon, J. *Tetrahedron Lett.* **1985**, *26*, 2399.

(18) Foxman, B.; Marten, D.; Rosan, A.; Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2160.

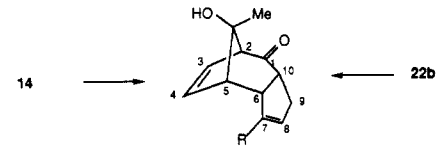
(19) Johnson, M. D.; Mayle, C. *Chem. Commun.* **1969**, 192.

(20) Cutler, A.; Ehnthholt, D.; Lennon, P.; Nicholas, K.; Marten, D. F.; Madhavarao, M.; Raghu, S.; Rosan, A.; Rosenblum, M. *J. Am. Chem. Soc.* **1975**, *97*, 3149.

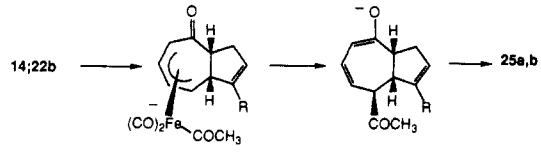
(21) Büchi, G.; Macleod, W. D.; Padilla, O. J. P. *J. Am. Chem. Soc.* **1964**, *86*, 4438.

(22) MM2 and MMX, used on a VAX, was obtained from Serena Software, 489 Serena Lane, Bloomington, IN. Updated versions of MODEL, obtained from Professor Midland, University of California, Riverside, and Professor Steliou, University of Montreal, were used for structure input and analysis.

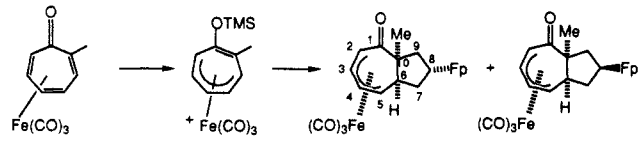
(23) Semmelhack, M. F.; Herndon, J. W. *J. Organomet. Chem.* **1984**, *265*, C15.

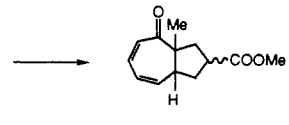


entially with a coordinated carbonyl group. This reaction manifold leads through migratory insertion to 3-cyclohexenyl ketones.[24] In the present circumstance, these transformations may be depicted as proceeding similarly through the formation of the anionic acyl complex **26**. Migratory insertion of the acyl ligand and subsequent loss of the iron carbonyl group releases the dienolate anion **27**, which undergoes intramolecular aldol condensation to give the observed product.



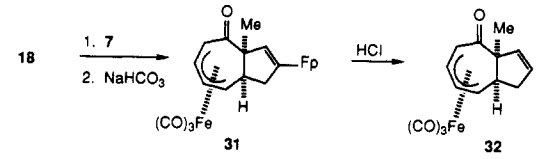
We next turned to an examination of the parallel reactions of cations derived from methylated cycloheptatrienoneiron tricarbonyl complexes with Fp complexes. Of these, 2-methyltroponeirone tricarbonyl seemed particularly attractive, since its cycloaddition reactions could provide entry to the pseudoguaiane skeleton. Silylation of 2-methyltroponeiron tricarbonyl[25] was carried out as before with trimethylsilyl triflate in methylene chloride at −78 °C, and the resulting tautomeric mixture of tropyliumiron complexes was treated with (η^1-allyl)Fp. The two products formed in this reaction in a ratio of 1:2.2 (69%) were easily separated and are assigned as the syn and anti cycloadducts **29a** and **b**. Each shows the pattern of ^{13}C resonances characteristic of an unsubstituted cycloheptadieneiron tricarbonyl unit, and their proton NMR spectra show singlet resonances at δ 1.08 and 1.00, respectively, for the angular methyl group. The stereochemical assignments at C-8 are based on a comparison of the ^{13}C chemical shifts for the methine carbon center at C-8 and the methyl carbon center attached to C-10, both of which exhibit τ-shielding effects due to either the methyl or Fp substituents. Thus, the methyl resonance is at higher field in **29a** compared with **29b**, while the C-8 carbon resonance is more shielded in **29b** compared with **29a**. Degradation of the mixture of cycloadducts by treatment with ceric ammonium nitrate in methanol solution gave the ester **30** in high yield. The formation of **29** from 2-methyltropone suggests that the reactive tropyliumiron carbonyl tautomer must have structure **28**, in which both substituents are on the uncomplexed double bond. Such a tautomer might be expected to predominate at equilibrium, since the ligand substituents are at positions of least steric interaction with the iron tricarbonyl group. As in the reactions of **7**, nucleophile attack on **28** takes place preferentially at the pentadienyl terminus, β to the silyloxy substituent.



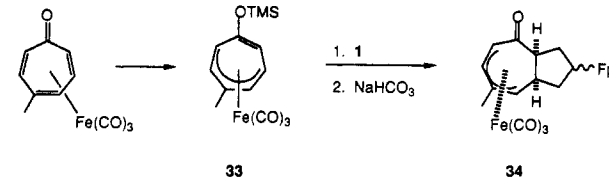


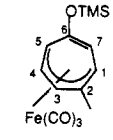
(24) Semmelhack, M. F.; Herndon, J. W. *Organometallics* **1983**, *2*, 363.
(25) Eisenstadt, A. *J. Organomet. Chem.* **1975**, *97*, 443.

The reaction of (η^1-allenyl)Fe (**18**) with silylated 2-methyltroponeiron tricarbonyl also gave a single cycloadduct **31**, in moderate yield, and this, unlike **20**, was selectively demetalated to give only a single product **32** in 81% yield.



The cycloaddition reaction of 4-methyltroponeiron tricarbonyl with (η^1-allyl)Fp provides an interesting counterpoint to the above results. Our interest in this complex lay in its potential use as a precursor to the large family of guaianolides. The free ketone was prepared from *p*-methylanisole following a procedure employed earlier by Birch and Keeton[26] for the synthesis of 4-isopropyltropone and was converted to its iron tricarbonyl complex by treatment with iron enneacarbonyl. Of the tautomeric cationic complexes formed on treatment of 4-methyltroponeiron tricarbonyl with TMS triflate, cations **33** and **35** would be expected to be product determining. Of these, the earlier findings of Brookhart, Harris, and Davis[13] would appear to favor **35** as the predominant species at equilibrium. In the event, treatment of silylated 4-methyltroponeiron tricarbonyl with (η^1-allyl)Fp gave only **34** as a mixture of C-8 epimers, the product anticipated from the reaction of **33** alone. The failure of tautomer **35** to undergo cycloaddition may be due to steric retardation by the methyl group of nucleophile addition to C-1. The structural assignment for **34** is made on the basis of an analysis of its NMR spectrum, especially the ^{13}C attached proton test, which shows that one of the *internal* carbon centers of the complexed dieneiron tricarbonyl unit is quaternary. These results would appear to foreclose the use of 4-substituted troponeiron tricarbonyls as precursors to guaianolides.





Conclusion

The reactions of trimethylsilyloxy or di-*n*-butylboryloxytropyliumiron tricarbonyl salts with allyl-, propynyl-, and allenylFp complexes provide a unique and facile entry to hydroazulenes functionalized in both the seven- and five-membered rings. A further examination of these cycloaddition reactions and the elaboration of the resulting cycloadducts is planned.

Experimental Section

Solvents were routinely dried by standard procedures and stored under nitrogen or argon. All reactions and subsequent operations were performed under nitrogen or argon.

Infrared spectra were recorded on Perkin-Elmer spectrophotometers, Models 457, 567, and 683. Proton magnetic resonance, PMR, were recorded on Perkin-Elmer R-32 (NSF GU 3852), Varian EM-390, or Varian XL-300 (NSF GU 3852). Carbon-13 NMR spectra were recorded on either a Bruker WH-90 at 22.64 MHz (NSF GU 3852 GP 37156) or a Varian XL-300 at 75.28 MHz and were collected with broad band proton decoupling for determination of chemical shifts and with the APT program to determine multiplicities.

Melting points were determined under a nitrogen atmosphere on a Kofler hot stage and are uncorrected.

Elemental analyses were determined by either Galbraith Laboratories, Inc., Knoxville, TN or Microlytics, South Deerfield, MA.

(26) Birch, A. J.; Keeton, R. *J. Chem. Soc. C* **1968**, 109.

Preparation of Troponeiron Tricarbonyl. Cycloheptatrienone[27] (1.095 g, 10.32 mmol) and $Fe_2(CO)_9$ (8.56 g, 23.5 mmol) were warmed together in 20 mL of degassed benzene at 55 °C for 90 min under N_2 in the dark. The solution was allowed to cool and was then chromatographed directly on a 3-in. column of alumina (neutral, activity 3). The first fraction ($Fe_3(CO)_{12}$) was discarded. The product was eluted as a deep red-orange band with 50/50 CH_2Cl_2/skellysolve-B. Removal of solvent gave 2.46 g (96%) of troponeiron tricarbonyl: mp 70–71 °C, lit. 71–72 °C:[28] IR (CH_2Cl_2) 2020, 2001, 1950, 1637 cm^{-1}; ^1H NMR ($CDCl_3$) 6.58 (m, 1 H, H-6), 6.39 (m, 2 H, H-3, 4), 5.05 (m, 1 H, H-7), 3.19 (m, 1 H, H-2), 2.75 (m, 1 H, H-5).

Preparation of Cycloadduct 9. Troponeiron tricarbonyl (0.204 g, 0.83 mmol) was taken up in 5 mL of methylene chloride in a 25-mL reaction flask. The system was flushed with Ar and cooled to −78 °C, and 0.82 mmol of freshly distilled TMS triflate solution in CH_2Cl_2 was added via syringe. The color of the solution changed instantly from a bright red to dark brown. After 3 h the reaction was complete, as evidenced by the disappearance of infrared absorptions at 2058 and 1985 cm^{-1} and the formation of two new bands at 2040 and 2095 cm^{-1}. (η^1-allyl)Fp (0.267 g, 1.22 mmol) was then added via syringe, and the temperature was maintained at −78 °C for an additional hour, during which time a yellow precipitate formed. The solution was allowed to come to room temperature and was then refluxed for 3 h. After cooling, solvent was removed, and the crude product was taken up in 10 mL of THF containing 4 mL of saturated aqueous $NaHCO_3$. The mixture was stirred for 30 min and then worked up by extraction with ether. After drying over $MgSO_4$, and removal of solvent, a red-orange oil remained, which was directly chromatographed on silica gel eluting with 2.5:1 hexane/EtOAc. This yielded 0.225 g of cycloadduct **9** (59%) as a yellow powder: mp 143.5–144 °C dec; IR (CH_2Cl_2) 2090, 1930, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.55 (m, 2 H, H-3, 4), 4.64 (s, 5 H, Cp), 3.09–1.60 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 209.75 (C-1), 64.10, 56.44 (C-2), 91.65, 91.34 (C-3), 89.69, 89.05 (C-4), 53.71, 56.12 (C-5), 50.00 (C-6), 46.89 (C-7), 16.16 (C-8), 43.31 (C-9), 52.21 (C-10), 85.15 (Cp), 208.84 (Fe-CO), 216.76 (Fp-CO). Anal. Calcd for $C_{20}H_{16}O_6Fe_2$: C, 51.76; H, 3.45. Found: C, 51.33; H, 3.62.

Preparation of Cycloadduct 17. Troponeiron tricarbonyl (0.218 g, 0.89 mmol) in methylene chloride solution cooled to −78 °C was treated with *n*-Bu_2BOTf (0.89 mmol). After 3 h, 1.21 equivs (0.251 g, 1.08 mmol) of a mixture of *cis*- and *trans*-1-Fp-2-butene[16] was added neat at −78 °C. The reaction was continued at this temperature for an additional hour. During this time, a precipitate formed but dissolved upon warming the solution to reflux. Reaction was continued at this temperature for 3 h. Solvent was then removed, and the residue was taken up in 20 mL of THF containing 5 mL of saturated aqueous $NaHCO_3$ and allowed to stir for 30 min. Workup by ether extraction, followed by removal of solvent left the product as a red-orange oil. This was chromatographed on a silica gel preparative TLC plate with 2:1 hexane/EtOAc to give 0.322 g (62%) of cycloadduct **17**, a mixture of diastereomers, as a yellow oil: IR (CH_2Cl_2) 2095, 1980, 1936, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.70 (m, 2 H, H-3,4), 4.75 (s, 5 H, Cp), 3.05–1.50 (m, 8 H), 1.10 (d, J = 6 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) 208.7 (C-1), 67.81, 65.59 (C-2), 92.04, 90.80 (C-3), 90.15, 89.50 (C-4), 59.94, 59.55 (C-5), 57.48, 56.50 (C-6), 54.36, 53.90 (C-7), 16.09 (C-8), 53.38, 48.77 (C-9), 59.29, 58.71 (C-10), 85.73, 85.34 (Cp), 44.41 (Me), 208.90 (Fe-CO), 216.96 (Fp-CO). Anal. Calcd for $C_{21}H_{18}O_6Fe_2$: C, 52.71; H, 3.76. Found: C, 52.71; H, 3.62.

Preparation of Cycloadduct 12. Troponeiron tricarbonyl (0.419 g, 1.70 mmol) was taken up in methylene chloride, and the solution was cooled to −78 °C. *n*-Bu_2BOTf (1.70 mmol) was added to this and the reaction was allowed to proceed for 3 h. 1-Fp-2-butyne (2.244 g, 9.75 mmol), dissolved in 15 mL of methylene chloride and cooled to −78 °C, was then added via cannula. The reaction was maintained at this temperature for 1 h and was then warmed to reflux for 3 h. After cooling to room temperature, approximately 0.5 g of K_2CO_3 and 5 mL of absolute EtOH was added, and the reaction was allowed to proceed for 3 h. The solution was then filtered through Celite and concentrated to dryness, and the residue was chromatographed on a 22 × 3 cm silica gel column with 1:1 skellysolve-B/EtOAc. Two products were collected, **12** (0.744 g, 92% yield), as a viscous yellow oil and 2-Fp-*p*-xylene (0.254 g) as a thermally labile, tan oil: IR of **12** (CH_2Cl_2) 2080, 1995, 1960, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) 5.78 (m, 1 H, H-3), 5.45 (m, 1 H, H-4), 4.80 (s, 5 H, Cp), 3.40–2.21 (m, 6 H, H-2, 5, 6, 9, 10), 1.85 (dd, J = 3, 4 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) 209.09 (C-1), 62.09 (C-2), 91.39, 89.24 (C-4), 63.84 (C-5), 53.71 (C-6), 147.38 (C-7), 96.91 (C-8), 53.12 (C-9), 58.13 (C-10), 84.95 (Cp), 17.39 (Me), 208 (M-CO), 216.52 (Fp-CO); IR of 2-Fp-*p*-xylene (CH_2Cl_2) 2010, 1960 cm^{-1}; ^1H NMR ($CDCl_3$) 7.45 (s, 1 H), 6.95 (d, J = 9 Hz, 1 H), 6.70 (d, J = 9 Hz, 1 H), 4.84 (s, 5 H, Cp), 2.40 (s, 3 H), 2.20 (s, 3 H). Anal. Calcd for $C_{21}H_{16}O_6Fe_2$ (**12**): C, 52.84; H, 3.35. Found: C, 52.12; H, 3.87. Anal. Calcd for $Cl_5H_{14}O_2Fe$ (15) (2-Fp-*p*-xylene): C, 63.86; H, 4.96. Found: C, 64.70; H, 5.79.

Preparation of Cycloadduct 14. Complex **12** (1.13 g) was dissolved in 60 mL of MeOH and 15 mL of 1% HCl was added. After 4 h at room temperature, the crude product was subjected to flash chromatography (3 × 8 in. column, 3:1 skelly B/EtOAc) to give 0.617 g (87%) of **14**: IR (CH_2Cl_2) 2090, 1985, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) 5.70 (dt, J = 2, 5.5 Hz, 1 H, H-3), 5.45 (dt, J = 2, 5.5 Hz, 1 H, H-4), 5.15 (d, J = 4 Hz, 1 H, H-8), 3.25 (m, 3 H), 2.80 (m, 1 H), 2.25 (m, 2 H), 1.75 (t, J = 2 Hz, CH_3); ^{13}C NMR ($CDCl_3$) 208.12 (C-1), 61.50 (C-2), 91.97 (C-3), 89.76 (C-4), 58.91 (C-5), 58.01 (C-6), 145.56 (C-7), 122.17 (C-8), 52.34 (C-9), 58.45 (C-10), 35.77 (Me), 208.1 (Fe-CO). Anal. Calcd for $C_{14}H_{12}O_4Fe$: C, 56.02; H, 4.00. Found: C, 55.93; H, 4.23.

Preparation of Cycloadduct 20. Troponeiron tricarbonyl (0.221 g, 0.90 mmol) and *n*-BuBOTf (0.90 mmol) in methylene chloride were allowed to react for 3 h at −78 °C, following standard practice, and then 1.589 g (7.35 mmol) of 1-Fp-1,2-propadiene,[29] in 10 mL of methylene chloride, cooled to −78 °C, was added via cannula. The reaction was continued at this temperature for 1 h, and the solution was then warmed to reflux for 3 h. After cooling to ambient temperature, approximately 0.5 g of K_2CO_3 and 5 mL of absolute EtOH were added, the mixture was allowed to stir for 3 h, then filtered through Celite, and concentrated to dryness. The residue was chromatographed by the dry column technique on basic alumina (activity 3, 400 g), eluting with 2:1 skellysolve B/EtOAc to give 0.227 g (55%) of **20** as a tan powder: mp 190–191 °C dec; IR (CH_2Cl_2) 2085, 2015, 1990, 1960, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) 5.70–5.20 (m, 2 H, H-3, 4), 4.80 (s, 5 H, Cp) 3.30–2.05 (m, 7 H); ^{13}C NMR ($CDCl_3$) 209.5 (C-1), 63.26 (C-2), 91.23 (C-3), 89.10 (C-4), 61.04 (C-5), 50.91 (C-6), 58.29 (C-7), 135.79 (C-8), 143.88 (C-9), 60.20 (C-10), 84.97 (Cp), 208.99 (Fe-CO), 215.8 (Fp-CO). Anal. Calcd for $C_{20}H_{14}O_6Fe_2$: C, 51.98; H, 3.03. Found: C, 52.74; H, 3.03.

Preparation of Cycloadduct 22b. Troponeiron tricarbonyl (0.197 g, 0.801 mmol) and TMSOTf (0.80 mmol) were allowed to react in methylene chloride solution at −78 °C for 3 h, and then freshly chromatographed *cis*-3-ethoxy-1-Fp-propene[30] (**23**) was added in 10 mL of methylene chloride solution cooled to −78 °C via cannula. Instantly a yellow precipitate formed, which dissolved upon warming to room temperature and then reappeared during the 3-h reflux period. The crude reaction mixture was treated with 0.5 g of K_2CO_3 and 5 mL of absolute EtOH in 20 mL of methylene chloride for 3 h, filtered through Celite, and concentrated to dryness. The residue was chromatographed on silica gel eluting with 2:1 skellysolve-B/EtOAc to give 0.145 g (63%) of **22b** as a yellow oil and 0.026 g (7%) of **24** as a yellow foam: IR of **22b** (CH_2Cl_2) 2060, 1995, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) 5.75 (m, 2 H, H-3,4), 5.62 (m, 1 H, H-7), 5.44 (m, 1 H, H-8), 3.56 (m, 1 H), 3.20 (m, 2 H), 2.75 (m, 1 H), 2.36 (m, 2 H); ^{13}C NMR ($CDCl_3$) 216.00 (C-1), 62.05 (C-2), 91.55 (C-3), 89.44 (C-4), 57.87 (C-5), 55.35 (C-6), 128.00 (C-7), 136.47 (C-8), 35.98 (C-9), 50.74 (C-10), 208.62 (Fe-CO); IR of **24** (CH_2Cl_2) 2042, 1990, 1949, 1629 cm^{-1}; ^1H NMR ($CDCl_3$) 5.72 (t, J = 6.35 Hz, 1 H, H-3), 5.60 (t, J = 6.84 Hz, 1 H, H-4), 4.75 (s, 5 H, Cp), 3.54 (q, J = 7.0 8 Hz, 2 H, OCH_2), 3.33–2.91 (m, 6 H), 1.81 (dt, J = 9.6, 9.2 Hz, 2 H, H-9), 1.12 (t, J = 7.08 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) 210.22 (C-1), 62.08 (C-2), 91.75 (C-3), 89.52 (C-4), 57.12 (C-5), 55.94 (C-6), 96.16 (C-7), 15.20 (C-8), 43.11 (C-9), 50.39 (C-10), 64.51 (OCH_2), 21.51 (Me), 208.84 (Fe-CO), 217.39 (Fp-CO). Anal. Calcd for $C_{13}H_{10}O_4Fe$ (**22b**): C, 54.57; H, 3.50. Found: C, 54.21; H, 3.52. Anal. Calcd for $C_{22}H_{20}O_7Fe_2$ (**24**): C, 52.53; H, 3.01. Found: C, 52.42, H, 3.23.

Preparation of Cycloadducts 22a and 22b. Cycloadduct **20** was taken up in 20 mL of THF and treated with 4 mL of 10% HCl for 2 h at ambient temperature. The reaction was then poured into 20 mL of diethyl ether and 20 mL of brine. The aqueous phase was extracted with ether, and the combined organic phase was washed with saturated $NaHCO_3$ and then dried over $MgSO_4$. The residue, following removal of the solvent, was chromatographed on a silica gel prep TLC plate with 2:1 skellysolve-B/EtOAc to give 0.103 g (82%) of a 1:2 mixture of complexes **22a** and **22b** as determined by spectral comparison with pure **22b**. A ^{13}C NMR lanthanide shift experiment with Eu(fod)$_3$ on the mixture resulted in induced chemical shifts of 0.78, 0.71, and 2.27 ppm for C-7, -8, and -9, respectively, of the major isomer, while the corresponding shifts observed for the minor isomer were 0.80, 0.70, and 2.57 for these centers: IR of **22a** (CH_2Cl_2) 2048, 1992, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) 5.74 (m, 4 H), 5.45 (m, 2 H), 3.61 (m, 1 H), 3.40 (m, 1 H), 3.18 (m, 3 H), 2.95 (m, 1 H), 2.82–2.50 (m, 2 H), 2.45–2.10 (m, 3 H); ^{13}C NMR ($CDCl_3$) 208.3 (C-1), 62.19 (C-2), 91.71 (C-3), 89.57 (C-4), 58.11 (C-5), 50.94 (C-6), 43.95 (C-7), 129.42 (C-8), 130.53 (C-9), 55.56 (C-10), 208.54 (M-CO). Anal. Calcd for $C_{13}H_{10}O_4Fe$: C, 54.57; H, 3.50. Found (for mixture): C, 54.78, H, 3.88.

Preparation of 25a. Cycloadduct **22b** 0.053 g (0.179 mmol) was dissolved in 8 mL of ether and cooled to −78 °C. Lithium dimethyl

(27) Radlick, P. *J. Org. Chem.* **1964**, *29*, 960.

cuprate (1.5 equivs) in 5 mL of ether was added via cannula, resulting in the immediate formation of a precipitate. The reaction mixture was stirred for 90 min at −78 °C, then warmed to room temperature, and poured into 20 mL of brine, and sufficient 10% HCl was added to cause the precipitate to dissolve. Workup and removal of solvent left a solid, which was chromatographed on a silica gel preparative plate with 10:1 CH_2Cl_2/MeOH to give the product (0.030 g, 88%) as a colorless solid: mp 84–85 °C; IR (CH_2Cl_2) 3590, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) 6.13 (dd, J = 6.2, 3.2 Hz, 1 H, H-4), 5.66 (m, 3 H, H-1, -2, -5), 3.35 (m, 1 H), 3.10 (m, 1 H), 2.88 (d, J = 3.2 Hz, 1 H, H-2), 2.52 (dd, J = 3.2, 4.25 Hz, 1 H, H-5), 2.26 (m, 2 H), 1.49 (s, 3 H, Me); ^{13}C NMR ($CDCl_3$) 210.31 (C-1), 65.3 (C-2), 131.21 (C-3), 128.76 (C-4), 45.53 (C-5), 47.58 (C-6), 139.83 (C-7), 129.65 (C-8), 39.18 (C-9), 50.31 (C-10), 26.01 (C-11), 85.35 (C-12). Anal. Calcd for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33. Found: C, 74.98; H, 8.31.

Preparation of 25b. The reaction of cycloadduct **14** (0.104 g, 0.348 mmol) with lithium dimethyl cuprate followed the procedure employed in the similar reaction of cycloadduct **22b**. The product obtained in 82% yield was a colorless oil: IR (CH_2Cl_2) 3590, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) 6.06 (dd, J = 7.1, 3.1 Hz, 1 H, H-4), 5.67 (dd, J = 7.1, 2.9 Hz, 1 H, H-3), 5.23 (br s, 1 H, H-8), 3.13 (m, 2 H, H-6), H-10), 2.88 (d, J = 3.1 Hz, 1 H, H-2), 2.60 (dd, J = 2.9, 4.2 Hz, 1 H, H-5), 2.34 (m, 1 H, H-9), 1.72 (s, 3 H, Me) 1.51 (s, 3 H, Me); ^{13}C NMR ($CDCl_3$) δ 210.65 (C-1), 65.54 (C-2), 139.19 (C-3), 122.69 (C-4), 48.44 (C-5), 48.65 (C-6), 139.62 (C-7), 129.86 (C-8), 38.5 (C-9), 48.84 (C-10), 26.09 (C-11, Me), 85.30 (C-12), 14.97 (C-13, Me). Anal. Calcd for $C_{12}H_{16}O_2$: C, 75.73; H, 8.74. Found: C, 75.77; H, 8.70.

Preparation of 2-methyltropone.[31] Freshly distilled cyclopentadiene (10.25 g, 0.16 mol) and dry triethylamine (18.21 g, 0.18 mol) were dissolved, under a nitrogen atmosphere in 100 mL of *n*-hexane in a 500-mL, three-necked flask fitted with an overhead stirrer and thermometer. After cooling to 0 °C, 2-chloropropionyl chloride (19.72 g, 0.16 mol) in 25 mL of *n*-hexane was added slowly via syringe to the diene and amine solution. Vigorous stirring was maintained to keep the temperature between 0 and 5 °C. Following addition, the reaction was allowed to come to room temperature, triethylammonium chloride was removed by filtration, and the hexane solution was washed with water, then aqueous acid, and finally aqueous sodium bicarbonate to neutrality. The hexane solution was dried over magnesium sulfate, and solvent was removed in vacuo. PMR spectral analysis revealed a 2.6:1 ratio of diastereomers which were separated by distillation to yield 6.61 g (0.042 mol) of the *exo*-methylcyclobutanone (bp 78–80 °C/6 mm; lit. 69 °C/2 mm). The exo isomer could not be obtained in pure form by this procedure, but it was undesired in any case. The endo isomer was solvolyzed at reflux in 150 mL of a stock solution of NaOAc/HOAc (200 g, NaOAc·$3H_2O$ in 800 mL of glacial HOAc and 300 mL of H_2O). IR analysis of aliquots allowed the progress of the reaction to be followed. After 24 h, the reaction was brought to pH = 10 with 30% aqueous NaOH and extracted with four 100-mL portions of chloroform. The combined extracts were dried over calcium chloride, concentrated at reduced pressure, and then kuhgelrohr distilled (105 °C/0.1 mm) to give 2.27 g (0.019 mol, 45% yield from cyclobutanone adduct) of 2-methyltropone: IR (CH_2Cl_2) 1630, 1575 cm^{-1}; ^1H NMR ($CDCl_3$) 2.1 (s, 3 H), and 6.9 (m, 5 H).

Preparation of 2-Methyltropone $Fe(CO)_3$. The 2-methyltropone (1.20 g, 10.13 mmol) was complexed following the procedure outlined for the preparation of the parent compound. The new complex was isolated as deep red plates: mp 64 °C; lit.[25] 63.5–64.5 °C (2.23 g, 84%); IR (CH_2Cl_2) 2058, 1985 cm^{-1}; ^1H NMR ($CDCl_3$) 6.40 (m, 3 H, H-3, -5, -6), 3.20 (m, 1 H, H-7), 2.71 (m, 1 H, H-4), 1.50 (s, 3 H, CH_3).

Preparation of Cycloadduct 29a,b. 2-Methyltroponeiron tricarbonyl (0.261 g, 1.00 mmol) was silylated in the usual manner with freshly distilled TMSOTf in methylene chloride at −78 °C, and (η^1-allyl)Fp (0.374 g, 1.71 mmol) was added. The reaction was maintained at −78 °C for 1 h, then allowed to warm to ambient temperature, and was finally heated at reflux for 3 h. After cooling to room temperature, solvent was removed and replaced with 10 mL of THF and 5 mL of saturated $NaHCO_3$, and the mixture was stirred for 45 min. Workup gave an orange-red oil which was chromatographed on a silica gel column with 2:1 skelly-B/EtOAc to give the product (0.303 g 65%), a yellow oil, as a mixture of diastereomers. The mixture was separated on a silica gel preparative plate, eluting with 3:1 skelly-B/EtOAc to give 0.208 g of the anti isomer **29b** and 0.096 g of the syn isomer **29a**: IR (CH_2Cl_2) (**29b**) 2080, 1990, 1940, 1631 cm^{-1}; ^1H NMR ($CDCl_3$) 5.70 (m, 2 H, H-3,4), 4.72 (s, 5 H, Cp), 3.20–2.70 (m, 4 H), 2.30–1.70 (m, 4 H), 1.08 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) 209.9 (C-1), 63.60 (C-2), 90.58 (C-3), 89.53 (C-4), 58.05 (C-5), 60.51 (C-6), 53.07 (C-7), 16.54 (C-8), 50.95 (C-9), 54.03 (C-10), 26.42 (C-11 methyl), 85.22 (Cp), 209.5 (Fe-CO), 217.02 (Fp-CO); IR (CH_2Cl_2) (**29a**) 2080, 1990, 1940, 1631 cm^{-1}; ^1H NMR ($CDCl_3$) 5.65 (m, 2 H, H-3,4), 4.68 (s, 5 H, Cp), 3.20–2.50 (m, 4 H), 2.0–1.20 (m, 4 H), 1.00 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) 210.0 (C-1), 66.64 (C-2), 91.82 (C-3), 89.14 (C-4), 59.56 (C-5), 57.81 (C-6), 53.84 (C-7), 19.72 (C-8), 53.68 (C-9), 55.37 (C-10), 24.67 (C-11 methyl), 85.25 (Cp), 209.5 (Fe-CO), 217.1 (Fp-CO). Anal. Calcd for $C_{21}H_{18}O_6Fe_2$: C, 52.71; H, 3.76. Found **22b**: C, 52.67; H, 3.76. Found **22a**: C, 52.31; H, 3.84.

Preparation of 30. Oxidative Demetalation of 22a,b. Complex **29** (mixture of diastereomers) (0.369 g, 0.77 mmol) was dissolved in 40 mL of MeOH and cooled to 0 °C. The solution was stirred, while carbon monoxide was bubbled into the solution through a syringe needle. In one portion, ceric ammonium nitrate (5.52 g, 10.07 mmol) was added to the solution. The reaction was maintained at 0 °C for 1 h and then raised to room temperature for an additional hour. Workup and chromatography of the product on neutral alumina preparative plates and eluting with 3:1 skelly-B/ethyl acetate gave the product as a colorless oil. This was further purified by kuhgelrohr distillation at 0.1 mm and 70 °C to give 0.145 g (82%) of dieneone ester **30**: IR (CH_2Cl_2) 1725, 1685 cm^{-1}; ^1H NMR ($CDCl_3$) 6.4–5.90 (m, 4 H), 3.65 (s, 3 H, $COOCH_3$), 3.5–3.25 (m, 3 H), 3.0–2.77 (m, 2 H), 2.71–2.55 (m, 1 H), 2.20–2.12 (m, 1 H), 1.20 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) 202.47 (C-1), 138.12, 137.82 (C-2), 134.29, 133.91 (C-3), 130.03, 129.58 (C-4), 123.71, 123.45 (C-5), 48.73 (C-6), 32.41 (C-7), 37.49 (C-8), 39.89 (C-9), 56.38 (C-10), 22.07 (C-11, Me), 177.13 (C-12 COOR), 51.78 (C-13, OMe). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 70.87; H, 7.31.

Preparation of Cycloadduct 31. 2-Methyltroponeiron tricarbonyl (0.212 g, 0.815 mmol) was treated with TMSOTf (1 equiv) in methylene chloride for 3 h at −78 °C. A precooled solution of (η^1-propadiene)Fp (18) (1.037 g, 4.80 mmol) in 10 mL of methylene chloride was added via cannula. The reaction was maintained at this temperature for 1 h, then warmed to room temperature, and refluxed for 3 h. After cooling the solution to room temperature, 0.5 g of K_2CO_3 and 5 mL of absolute EtOH were added, and the mixture was stirred for 2 h. Solids were removed by filtration through Celite, and solvent was removed in vauo. Flash chromatography on silica gel using 3:1 skellysolve-B/EtOAc material gave the alkenyl complex **31** as a tan powder (0.2124 g, 55%); mp 187 °C; IR (CH_2Cl_2) 2045, 2005, 1980, 1950, 1631 cm^{-1}; ^1H NMR ($CDCl_3$) 5.72 (m, 1 H, H-3), 5.38 (m, 1 H, H-4), 5.00 (d, J = 0.98 Hz, 1 H, H-9), 4.81 (s, 5 H, Cp), 3.15 (dd, J = 7.5 Hz, 1 H, H-2), 2.99 (m, 1 H, H-5), 2.80 (m, 2 H, CH_2), 2.22 (br s, 1 H, H-6), 0.93 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) 209.27 (C-1), 64.24 (C-2), 88.72 (C-3), 92.45 (C-4), 63.50 C-5), 58.22 (C-6), 59.29 (C-7), 141.81 (C-8), 143.0 (C-9), 59.43 (C-10), 22.71 (Me), Cp 85.12 (Cp), 209.27 (Fe-CO), 215.45 (Fp-CO). Anal. Calcd for $C_{21}H_{16}O_6Fe_2$: C, 52.97; H, 3.36. Found: C, 52.67, H, 3.41.

Preparation of Cycloadduct 32. Complex **31** was demetalated employing the conditions used for **20** (10% HCl, THF, 2 h) at room temperature, to give **32** (81%) as a yellow oil: IR (CH_2Cl_2) 2085, 1985, 1630 cm^{-1}; ^1H NMR ($CDCl_3$) 5.70 (m, 2 H, H-3, -4), 5.39 (m, 1 H, H-8), 4.99 (m, 1 H, H-9), 3.12–2.80 (m, 3 H, H-2, -5, -6), 1.72 (m, 2 H, H-7), 0.90 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) 209 (C-1), 64.31 (C-2), 92.54 (C-3), 88.79 (C-4), 63.51 (C-5), 58.34 (C-6), 59.44 (C-7), 142.95 (C-8), 143.49 (C-9), 59.33 (C-10), 23.1 (Me), 209.1 (Fe-CO). Anal. Calcd for $C_{14}H_{12}O_4Fe$: C, 56.03; H, 4.00. Found: C, 55.95; H, 4.11.

Preparation of 4-Methyltropone. The procedure used follows that of Burch and Keeton for the preparation of 4-isopropyltropone.[26] Burch reduction of 4-methylanisole with sodium in liquid ammonia gave 1-methoxy-4-methyl-1,4-cyclohexadiene in 77% yield. The diene (14.14 g, 0.11 mol) was dissolved in 100 mL of *n*-hexane with potassium *tert*-butoxide (13.92 g, 0.12 mol) and cooled to −20 °C, and 9.4 mL (13.89 g, 0.12 mol) of $CHCl_3$ was added by syringe pump over a 20-min period. The cooling bath was then removed, and the reaction was stirred overnight. Workup gave a crude product shown to be a 1:1 mixture of product and starting material. The mixture was distilled thru a 5 in. glass-helices packed fractionating column to yield 8.73 g (36%) of the dichlorocyclopropane product bp 73 °C/0.1 mm. A portion of this product (2.055 g, 9.93 mmol) in 40 mL of absolute ethanol was added to a solution of 2 g of Ag_2O (8.63 mmol) in 14.2 g of 48% HBF_4, and the solution was refluxed for 5 h. Standard workup gave the crude product as a brown oil, which was distilled to give 1.0 g (82%) of 4-methyltropone: IR (CH_2Cl_2) 1637 cm^{-1}; ^1H NMR ($CDCl_3$) 6.90 (m, 5 H), 2.23 (s, 3 H). Anal. Calcd for C_8H_8O: C, 80.0, H, 6.66; Found: C, 79.89; H, 6.78.

Preparation of (4-Methyltropone)$Fe(CO)_3$. Complexation was carried out following the procedure used for the preparation of troponeiron tricarbonyl. The yellow orange semisolid product was obtained in 10% yield

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as an inseparable mixture of 4-methyltroponeiron tricarbonyl (major) and 5-methyltroponeiron tricarbonyl (minor): IR (CH_2Cl_2) 2045, 1985, 1634 cm^{-1}; ^1H NMR of 4-methyltroponeiron tricarbonyl ($CDCl_3$) 6.55 (dd, 1 H, J = 9.2, 12 Hz, H-6), 6.21 (d, J 9.2 Hz, 1 H, H-3), 4.95 (d, J = 12.2 Hz, 1 H, H-7), 2.95 (d, J = 9.2 Hz, 1 H, H-2), 2.66 (d, J = 9.2 Hz, 1 H, H-5), 2.48 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) 209.1 (Fe-CO), 198.98 (C-1), 57.57 (C-2), 90.88 (C-3), 113.03 (C-4), 54.54 (C-5), 148.27 (C-6), 121.84 (C-7); ^1H NMR of 5-methyltroponeiron tricarbonyl ($CDCl_3$) 6.95 (1 H, H-6), 6.10 (d, J = 8.3 Hz, 1 H, H-7), 5.32 (d, J = 8.3 Hz, 1 H, H-4), 1.48 (s, 3 H, CH_3). Anal. Calcd for $C_{11}H_8O_4Fe$: C, 50.80; H, 3.08. Found: C, 50.58; H, 3.25.

Preparation of Cycloadduct 34. The mixture of 4-methyl- and 5-methyltroponeiron tricarbonyl (0.095 g, 0.366 mmol) was treated with 1 equiv of TMSOTf at -78 °C in 1 mL of CH_2Cl_2 for 3 h. (η^1-allyl)Fp (0.1355 g, 0.621 mmol) was added neat via syringe, and the reaction was continued for an hour at -78 °C, then allowed to warm to room temperature, and finally heated at reflux for 3 h. Solvent was removed and replaced with 10 mL of THF and 5 mL of saturated aqueous $NaHCO_3$, and the mixture was stirred for 90 min. The reaction was poured into 30 mL of Et_2O and 30 mL of brine. Workup yielded an orange-red residue which was chromatographed on a silica gel preparative plate with 1.5:1 skellysolve-B/EtOAc to give 0.079 g (45%) of product as a yellow oil and as a mixture of diastereomers: IR (CH_2Cl_2) 2080, 1995, 1945, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) 5.65 and 5.58 (dd, J = 1.47, 7.33 Hz, 1 H, H-3), 4.77 and 4.75 (s, 5 H, Cp), 3.20-1.40 (m, 9 H); ^{13}C NMR ($CDCl_3$) 210 (C-1), 68.28/66.32 (C-2), 88.65/90.50 (C-3), 107.04/108.1 (C-4), 55.67/55.53 (C-5), 53.03 (C-6), 49.75 (C-7), 16.53 (C-8), 43.48 (C-9), 52.81 (C-10), 23.06/25.36 (C-11), 85.32/85.15 (Cp), 210.08 (Fe-CO), CO 217.4 (Fp-CO). Anal. Calcd for $C_{21}H_{18}O_6Fe_2$: 52.71; H, 3.76. Found: C, 52.46, H, 3.71.

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Lipophobic Effects on Photochemical and Photophysical Behavior of Molecules with Polar Chains in Nonpolar Solvents. Evidence for Intermolecular Aggregation and Self-Coiling

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Abstract: The emission spectra of naphthalene end-labeled poly(ethylene glycol) oligomers (N-P_n-N) in isopentane and hexane at different temperatures have been studied under stationary and nonstationary conditions. The photochemical dimerization of the end naphthalene groups of N-P_n-N has also been investigated. The results reveal that lipophobic interactions force single N-P_n-N chains to coil up at room temperature and push them together to form aggregates below -20 °C. The excimer emission dominates the fluorescence spectra of N-P_n-N at low temperature. The fluorescence depolarization measurements demonstrate the existence of energy migration inside aggregates. The glassy solutions of N-P_n-N in isopentane (77 K) show strong delayed excimer fluorescence and phosphorescence of triplet excimer. The photoirradiation yields both intermolecular and intramolecular dimerization products of the naphthalene groups. This work provides the first example to apply lipophobic interaction to expediting the formation of macrocyclic entities, including a 42-membered-ring product. The conformational difference between singlet and triplet excimers was confirmed by the experiments of formation and cleavage of the photodimers.

Introduction

In aqueous solution substances with nonpolar regions tend to associate so as to diminish the hydrocarbon-water interfacial area. This hydrophobic effect is a principal contributor to substrates binding in micelles or membranes.[1] Recent studies demonstrate that in aquaorgano binary mixtures hydrophobic interactions force molecules with long hydrocarbon chains to aggregate and self-coil.[2] The properties of these aggregates, including aggregation number, microscopic polarity, and microviscosity inside aggregates, have been investigated,[3] and self-coiling has been used to expedite the formation of macrocyclic entities from molecules with flexible chains.[4] Furthermore, it has been recently established that for linear polymers, the conformation of the polymer chain can be affected by hydrophobic interaction.[5] Curiously, "lipophobic effects" on the behavior of molecules with polar regions in nonpolar solvents were scarcely reported. Substances with poly(ethylene glycol) (PEG) chain have been widely used as surfactants. Since PEG chains play a hydrophilic role in surfactant molecules, one might expect that in nonpolar solvents lipophobic interactions could force single PEG chains to coil up or push them together and make them form aggregates. We wish to report that this is indeed the case for PEG oligomers in appropriate temperature ranges.

A variety of approaches have been employed to explore and examine the structural and dynamic features of molecular assemblies, including electron micrography, NMR, neutron scat-

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