SHELXTL.[30] Tabulations of atom coordinates, thermal parameters, bond lengths and angles are available as supplementary material.

Acknowledgment. We acknowledge grants from the Research Committee of the New Zealand Universities Grants Committee.

Registry No. **2**, 24402-96-8; **5**, 110097-65-9; **6**, 78-94-4; **7**, 96-33-3; **8**, 79-10-7; **9**, 107-13-1; **11**, 141-05-9; **14**, 106-51-4; **15**, 526-86-3; **16**, 130-15-4; **17**, 108-31-6; **18**, 941-69-5; **20**, 462-80-6; **21**, 542-92-7; **23**, 922-67-8; **24**, 762-42-5; **25**, 1972-28-7; **26**, 20116-64-7; **27**, 4233-33-4; **28**, 110097-66-0; **29**, 110116-43-3; **30**, 110097-67-1; **31**, 110097-68-2; **32**, 110097-69-3; **33**, 106499-32-5; **34**, 110097-70-6; **35**, 110097-71-7; **36**, 106499-31-4; **37**, 110097-72-8; **39**, 110171-14-7; **40**, 110097-73-9; **42**, 110171-15-8; **43**, 110097-74-0; **44**, 110097-75-1; **45**, 33773-13-6; **46**, 33724-42-4; **47**, 110097-76-2; **48**, 110171-16-9; **49**, 110097-77-3; **50**, 110097-78-4; **51**, 110171-17-0; 10-ethoxy-10-hydroxy-13,14-bis(ethoxycarbonyl)heptacyclo[10.2.2.1^{5,8}.0^{2,6}.0^{4,9}.0^{7,11}]heptadec-15-en-3-one, 110097-79-5.

Supplementary Material Available: ORTEP diagrams and tables of fractional coordinates, thermal parameters, bond distances, and bond angles for **5** and **47** and full assignments of ^{1}H and ^{13}C NMR spectra of the Diels-Alder adducts (17 pages). Ordering information is given on any current masthead page.

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Homochiral Pinene-Fused Cyclopentadienes. Synthesis and π-Facially Selective Course of Diels-Alder Cycloadditions and Metallocene Formation[1]

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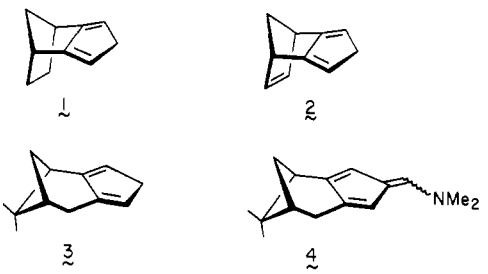
Received May 1, 1987

Homochiral (1*R*)-(−)-9,9-dimethyltricyclo[6.1.1.0^{2,6}]deca-2,5-diene (**3**) has been synthesized and its Diels-Alder reactions with *N*-phenylmaleimide, *p*-benzoquinone, dimethyl acetylenedicarboxylate, and (*Z*)-1,2-bis(phenylsulfonyl)ethylene investigated. As expected, [4 + 2] cycloaddition occurs preferably from the less-hindered π-surface, although to varying degrees. Reaction of **3** or the anion of **3** with $Fe(CO)_5$ and $TiCl_4$, respectively, is shown to provide only a single metallocene in each instance, complexation occurring from the direction syn to the methano bridge. The ligand transfer reactions of the 4-(dimethylamino)-substituted fulvene **4** with the hexafluorophosphates **29** and **35** gave rise to isomeric pairs of complexes. Above-plane coordination was again shown to predominate. Thus, **3** and **4** consistently undergo binding predominantly or exclusively from one π-face, in striking contrast to the behavior of isodicyclopentadiene (**1**) and isodicyclopentatriene (**2**).

Isodicyclopentadiene (**1**) and its dehydro derivative **2** were recognized several years ago to be plane-nonsymmetric dienes offering considerable latitude for the study of π-facial selectivity.[3-5] The remarkable stereochemical outcome of Diels-Alder,[6,7] [6 + 4],[8] and [3 + 4] cycloadditions[8b,9] to **1** has fostered controversy as to the root cause of the phenomena.[10-13] The course of metal complexation to these systems has also been documented.[1,14] More recently, appreciable attention has been directed toward other conjugated dienes with topologically dis-



1 2 3 4

(1) Paper 38 in the series dealing with isodicyclopentadienes and related molecules. For 37, see: Paquette, L. A.; McKinney, J. A.; McLaughlin, M. L.; Rheingold, A. L. *Tetrahedron Lett.* **1986**, *27*, 5599.
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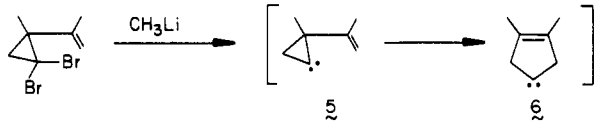
0022-3263/87/1952-4732$01.50/0

Scheme I



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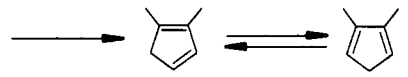
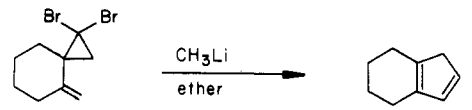
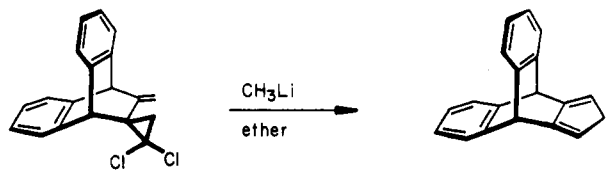


Scheme II



7 8



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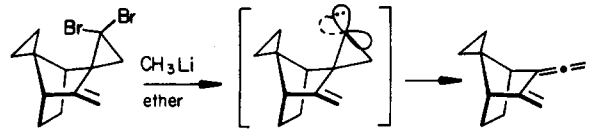
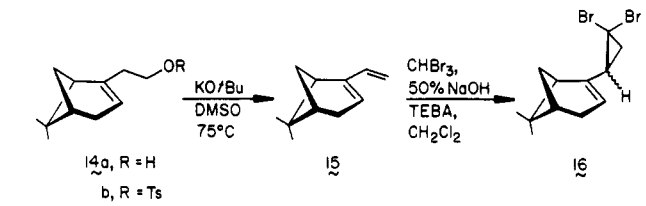


11 12 13

tinctive faces in an effort to define more precisely the factors that contribute to the synthetically useful stereoselectivity.[15-17]

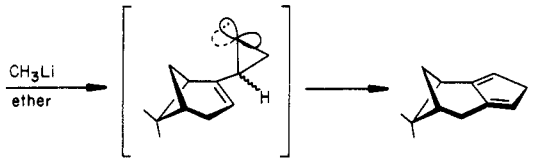
In this paper, we present observations that relate to **3** and **4**, two chiral, nonracemic, bicyclic-fused cyclopentadienes. While it is clear that the two π faces in **3** are distinguished sterically by virtue of geminal disubstitution on one of the bridges, its diene unit is not symmetrically disposed about the cyclobutane ring. The proximity to only one bridgehead C–H bond rather than to two (as in **1** and **2**) was expected to generate torsional energy differences of unknown, though expectedly smaller, magnitude,[12] to lessen substantially and perhaps curtail completely the π-orbital tilting believed to operate in **1** and **2**,[10] and to eliminate essentially all polarizability factors.[11] In these terms, **3** can be seen to differ appreciably from the norbornenyl and norbornyl analogues. Our interest in investigating the π-facially selective course of Diels–Alder cycloadditions to **3** and of metal coordination to **3** and **4** stem from these perceived distinctions.

Scheme III



14a, R = H
b, R = Ts

15 16



17 3

Table I. Comparative ^{1}H NMR Spectral Data for Cycloadducts 18–26 (300 MHz, $CDCl_3$ Solution, δ Values)

compd	endo CH_3	exo CH_3	$\Delta\delta_{CH_3}$, ppm	H_a (syn)
18	0.61	1.30	0.69	1.24
19	0.87	1.30	0.43	0.68
20	0.54	1.28	0.74	1.22
21	0.86	1.30	0.44	0.62
22	0.41	1.25	0.84	1.28
23	0.86	1.25	0.39	0.67
24	0.82	1.38	0.56	1.30
25	0.73	1.20	0.47	0.50
26	0.89	1.29	0.40	0.65

Results

Synthesis. The capability of (α-halocyclopropyl)lithium reagents to lose lithium halide and form singlet cyclopropylidenes (e.g., **5**) or their equivalent has been appreciated for some time.[18] When the three-membered ring carries a vinyl group, cyclopropylidene–cyclopentylidene (**6**) electronic reorganization may occur (Scheme I). This isomerization pathway, which has become known as the Skattebøl rearrangement,[19] ultimately leads to cyclopentadiene products. The conversion of **7** to **8**[20] and of **9** to **10**[21] are exemplary (Scheme II). However, when the associated ring system is strained to a greater extent as in **11**, only vinyl allenes such as **13** are formed.[6f,20] The rerouting away from cyclopentadiene formation would appear to reflect an inability on the part of the empty carbene p orbital in **12** to interact with the flanking double bond because of severe geometric constraints.[22,23]

If this hypothesis is correct, then the structural inhibition to carbene–carbene rearrangement should be fully alleviated by positioning the carbenoid center completely external to the bicyclic framework as in **17** (Scheme III).

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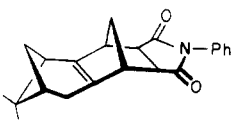
Accordingly, dibromocyclopropane **16** was targeted as the primary compound of interest. From among the various known methods to prepare (1*R*)-(+)-nopadiene (**15**), the decision was made to begin with commercially available (1*R*)-(−)-nopol (**14a**), since it proved possible to recrystallize its tosylate (**14b**) to optical purity. Subsequent base-promoted elimination according to Cupas and Roach[24] furnished the desired homochiral diene in good yield.

For the strategy to be successful, it was necessary that dibromocarbene react at the lesser substituted olefinic center in **15**. Although this reactivity pattern is contrary to that customarily followed by this reagent,[25] the bicyclo[3.1.1]heptene double bond in this instance is more sterically shielded on both of its surfaces than is the vinyl substituent. As expected, the sensitivity of dibromocarbene to steric factors caused cyclopropanation to occur exclusively as in **16**. 1,4-Addition was not seen.[26] Upon exposure to ethereal methyllithium at room temperature, both diastereomeric dibromides **16** were transformed efficiently into **3**.

Treatment of the lithium salt of **3** with the complex of dimethylformamide and dimethyl sulfate[27] afforded the 4-(dimethylamino)-substituted fulvene **4** as a 1:1 mixture of *E*/*Z* isomers.

Stereochemical Course of [4 + 2] Cycloadditions to 3. The Diels–Alder studies were carried out with several reagents recognized to possess varied dienophilic reactivity. In most of the reactions, the dimerization of **3** was seen to be modestly competitive with capture of the coreactant. Also, while one might reasonably expect concurrent addition to the several [1,5]-H shift isomers of **3**,[28] only traces of these adducts were seen and their characterization was not pursued.

Admixture of **3** with 1 equiv of *N*-phenylmaleimide in a benzene–hexane (10:1) solvent system at 25 °C led to the complete consumption of diene in 16 h. ^{1}H NMR analysis of the product mixture immediately following solvent evaporation revealed two adducts to be present in a 1:9 ratio. These isomers were readily separated by chromatography and identified as **18** and **19**, respectively, on the



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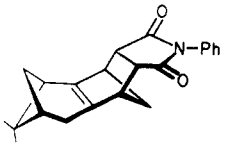
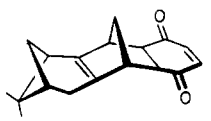


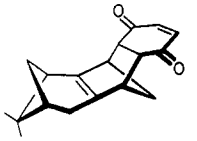
19

basis of their spectra. Two groups of signals were particularly diagnostic of stereochemical detail. Whereas the methyl singlets of **19** are seen to be separated by 0.43 ppm, those associated with **18** are more widely spaced ($\Delta\delta$ = 0.69 ppm, see Table I). This phenomenon is due entirely to upfield displacement of the inner methyl group in **18**, which we attribute to its penetration into the shielding region of the internal π bond. Norbornene double bonds are now well known to experience deformation in the endo direction,[15b,16c,29] particularly in *syn*-sesquinorbornenes.[5,6c,d,k,8b,c,30] Topological deformation in this sense can set the proper spatial proximity only in **18**. Otherwise, the >C*H*CO protons in both adducts appear as mutually coupled doublets with no evidence of spin–spin interaction with the neighboring bridgehead hydrogens, thereby indicating the maleimide ring to be configued exo in both instances.[31]

When **3** was allowed to stand with *p*-benzoquinone at room temperature for 24 h, a pair of adducts was produced in a 1:10 ratio. These were separated chromatographically and identified as **20** and **21**, respectively. The exo ori-



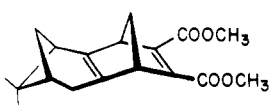
20



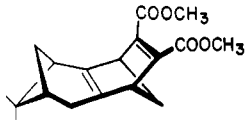
21

entation of the cyclohexenedione ring in both compounds was apparent from the singlet nature of the pair of bridgehead protons. The absence of coupling to the α-carbonyl hydrogens arises because of their endo disposition and approximately 90° dihedral angle relationship. Once again, the less dominant product exhibited the more widely spaced methyl singlets (Table I). The notably shielded nature of the inner methyl absorption in **20** is, as before, consistent only with its positioning on the endo surface of the norbornene double bond.

The use of dimethyl acetylenedicarboxylate gave rise to a 1:6 mixture of adducts. The structural features of the resulting dienes were established in much the same manner, with $\Delta\delta_{CH_3}$ for **22** (0.84 ppm) being double that for **23** (0.42 ppm).



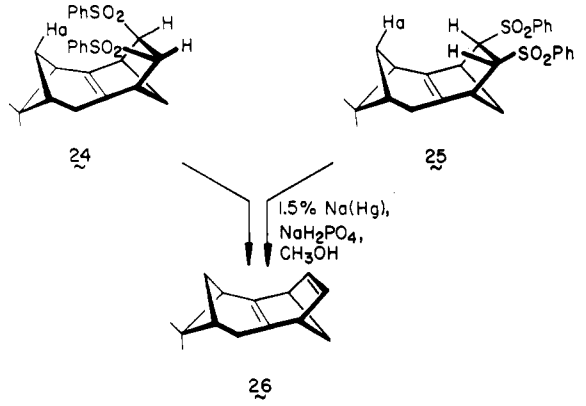
22



23

The cycloaddition with (*Z*)-1,2-bis(phenylsulfonyl)-ethylene[32] also led to a two-component product mixture (ratio 1:2.2). However, the disulfones so produced exhibited $\Delta\delta_{CH_3}$ values (0.47 and 0.56 ppm) that were not widely disparate and consequently did not conform to the precedent established in the three earlier examples. The underlying cause of this effect is that *both* **24** and **25** are the result of above-plane attack on **3**. It proved an easy matter to subject each adduct to reductive desulfonylation.[33] The identical hydrocarbon isolated from the two reactions exhibits a $\Delta\delta_{CH_3}$ of 0.40 ppm in complete agreement with its formulation as **26**. Assignment of exo stereochemistry to the phenylsulfonyl groups in major product **25** stems from the usual coupling constant measurements and the appearance of H_a (see formula) at δ 0.50.

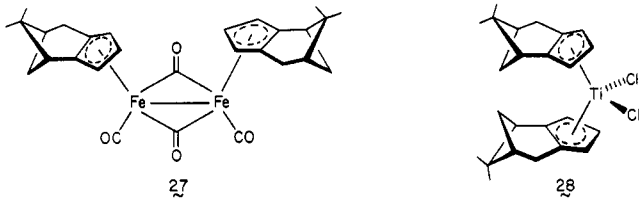
(24) Cupas, C. A.; Roach, W. S. *J. Org. Chem.* **1969**, *34*, 742.
(25) Moss, R. A. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; John Wiley and Sons, Inc.: New York, 1973; pp 153–304.
(26) (a) Mayr, H.; Heigl, U. W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 579. (b) Jennskens, L. W.; de Wolf, W. H.; Bickelhaupt, F. *Ibid.* **1985**, *24*, 585.
(27) This procedure is modeled after that described for cyclopentadiene: Hafner, K.; Vopel, K. H.; Ploss, G.; Koning, C. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 431.
(28) Minor amounts of these tautomers can be seen by ^{1}H NMR to be present in samples of **3** at room temperature. Their reactivity in [4 + 2] cycloadditions is obviously less than that of **3**.
(29) (a) Burnell, E. E.; Diehl, P. *Can. J. Chem.* **1972**, *50*, 3566. (b) Emsley, J. W.; Lindon, J. L. *Mol. Phys.* **1975**, *29*, 531. (c) Cole, K. C.; Gilson, D. F. R. *J. Mol. Struct.* **1982**, *82*, 71. (d) Pinkerton, A. A.; Schwarzenbach, D.; Stibbard, J. H.; Carrupt, P.-A.; Vogel, P. *J. Am. Chem. Soc.* **1981**, *103*, 2095. (e) Mackenzie, K.; Miller, A. S.; Muir, K. W.; Manojlovic-Muir, Lj. *Tetrahedron Lett.* **1983**, *24*, 4747.
(30) Bartlett, P. D.; Combs, G. L., Jr. *J. Org. Chem.* **1984**, *49*, 625.
(31) (a) Marchand, A. P.; Rose, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 3724. (b) Marchand, A. P. *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems*; Verlag Chemie International: Deerfield Beach, FL 1982.
(32) De Lucchi, O.; Lucchini, V.; Pasquato, L.; Modena, G. *J. Org. Chem.* **1984**, *49*, 596.
(33) Paquette, L. A.; Künzer, H.; Green, K. E.; De Lucchi, O.; Licini, G.; Pasquato, L.; Valle, G. *J. Am. Chem. Soc.* **1986**, *108*, 3453.



24 25 26

Projection of the sulfone substituents into regions of space surrounding H_a as in **24** introduces a deshielding element that is clearly evident (δ_{H_a} = 1.32).

Coordination of 3 to Metals. When **3** was heated with 3 molar equiv of iron pentacarbonyl in *n*-octane according to the general procedure of King and Bisnette,[34] complex **27** was obtained. However, the yield was disappointingly low (12.5%). In an attempt to improve matters, cyclooctene was added to serve as hydrogen acceptor. Matters improved to the 29.5% level. Subsequently, it was found that norbornene serves admirably well in this capacity and allows the isolation of **27** in 70% yield. These experimental findings lend substantial support to the cyclopentadienedicarbonyl hydride mechanistic hypothesis advanced some time ago by Pauson[35] and by Kochhar and Pettit.[36] The dark brown crystals of **27** proved amenable to X-ray crystallographic analysis.[37] Not only was it uncovered that coordination to iron occurs from the π-face proximal to the methano bridge but also that **27** crystallizes as the cis isomer.[38] The parent cyclopentadiene complex prefers to adopt trans geometry, although X-ray data are available for both cis[39] and trans forms.[40] In the present instance, no attempt has been made to assess the possible dynamic behavior of **27**.[41]



27 28

The cyclopentadienide anion of **3** reacted with titanium tetrachloride in ether to deliver **28** in 39% isolated yield. The three-dimensional features of this deep-red crystalline complex were again determined to be as illustrated by X-ray analysis.[42] The strong tendency for below-plane complexation on both ligands was once more made evident.

Conversion of 4 to Metallocene Derivatives. The purpose of this phase of the investigation was to assess the stereochemical course of ligand substitution by **4** on metal transfer reagents *under the conditions of light and heat*. (η^5-Cyclopentadienyl)(η^6-*p*-xylene)iron(II) hexafluorophosphate (**29**) and (η^5-cyclopentadienyl)tris(acetonitrile)ruthenium(II) hexafluorophosphate (**35**) have previously been utilized successfully for these purposes[14b,43-45] and were employed here. Irradiation of a solution of **4** and a slight excess of **29** in dichloromethane with a 250-W sunlamp for 24 h and subsequent alkaline hydrolysis gave rise to a 27:73 mixture of **30** and **31** (Scheme IV). It proved not feasible to separate these isomers chromatographically. Accordingly, the mixture was reduced with sodium borohydride to the corresponding alcohols **32** and **33**, which were individually obtained in a pure state and reoxidized to **30** and **31**, respectively, with manganese dioxide. The alcohols were found to be relatively unstable to traces of acid and to light. This was especially true in the case of **33**, which when dissolved in $CDCl_3$ deposited insoluble iron-containing decomposition products before an NMR spectrum could be successfully recorded. This complication could, however, be avoided by making recourse to C_6D_6 as solvent. When left exposed to laboratory light, once pure alcohols were rather quickly transformed into a multispot mixture as determined by TLC. When protected from light, **32** and **33** were indefinitely stable.

The major alcohol **33** was also transformed into dimeric ether **34** by reaction with 0.5 molar equiv of *p*-toluenesulfonyl chloride in the presence of triethylamine.

The stereochemical features of **30–34** were assigned on the basis of their ^{1}H NMR spectra (in C_6D_6 solution), particularly in relation to the chemical shifts of the pairs of hydrogen atoms and methyl groups on the one-carbon bridges. As in related molecules,[14b] the metal exerts a demonstrably strong deshielding influence on the syn,endo substituent. The appearance of the endo methyl singlet of **30** at δ 1.16 ($\Delta\delta_{CH_3}$ = 0.10 ppm) is very telling, particularly in relation to its more normal location in the spectrum of **31** (δ 0.43, $\Delta\delta_{CH_3}$ = 0.75 ppm). The situation is, of course, reversed for H_a, which appears at δ 0.61 in **30** and at δ 1.86 in **31**. This long-range anisotropy is evident as well in the dichlorotitanium complex **28** and is deemed to be entirely reliable as a diagnostic of stereochemistry. The assignments in the ruthenium series to follow are based as well on this deshielding phenomenon (Table II).

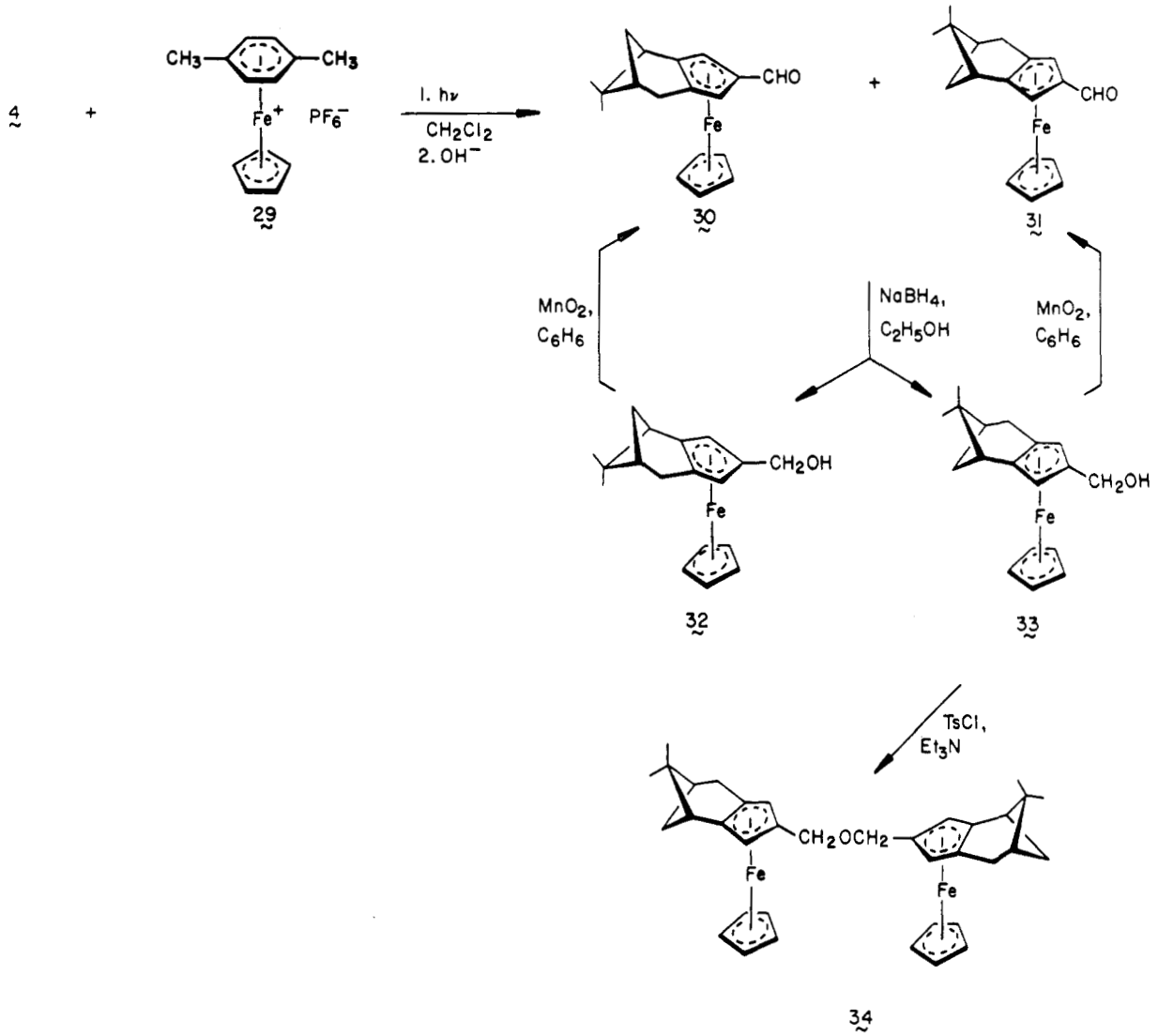
Table II. Comparative ^{1}H NMR Spectral Data for Metallocenes 30–33 and 36–39 (300 MHz, C_6D_6 Solution, δ Values)

compd	endo CH_3	exo CH_3	syn H
30	1.16	1.26	0.61
31	0.43	1.18	1.86
32	1.54	1.24	0.73
33	0.53	1.24	2.30
36	1.05	1.14	0.89
37	0.62	1.20	1.52
38	1.19	1.25	0.99
39	0.70	1.25	1.81

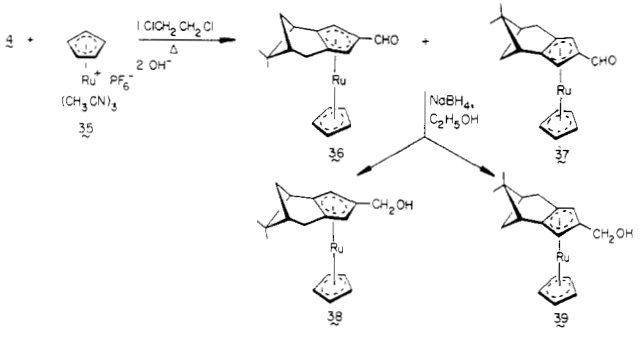
When **4** was heated with ruthenium(II) salt **35** in 1,2-dichloroethane, ligand transfer smoothly took place to provide a 7:93 mixture of **36** and **37** after alkaline hydrolysis (Scheme V). As before, the aldehyde mixture was reduced to the corresponding alcohols with ethanolic sodium borohydride. At this point, it proved an easy matter

(34) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1967**, *8*, 287.
(35) (a) Hallam, B. F.; Mills, O. S.; Pauson, P. L. *J. Inorg. Nucl. Chem.* **1955**, *1*, 313. (b) Pauson, P. L. *Proc. Chem. Soc.* **1960**, 297.
(36) Kochhar, P. K.; Pettit, R. *J. Organomet. Chem.* **1966**, *6*, 272.
(37) We thank Professor, A. L. Rheingold (University of Delaware) for this crystallographic structure determination.
(38) For a computer-generated perspective view of **27** derived from the X-ray analysis, consult ref 1.
(39) Mills, O. S. *Acta Crystallogr.* **1968**, *11*, 620.
(40) Bryan, R. F.; Greene, P. T.; Field, D. S.; Newlands, M. J. *J. Chem. Soc. D* **1969**, 1477.
(41) See: Gansow, O.; Burke, A. R.; Vernon, W. D. *J. Am. Chem. Soc.* **1972**, *94*, 2550.
(42) An ORTEP representation of **28** can be found in ref 1.
(43) (a) Sutherland, R. G. *J. Organomet. Chem. Libr.* **1977**, *3*, 311. (b) Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1980**, *19*, 3007. (c) Lee, C. C.; Gill, U. S.; Iqbal, M.; Azogu, C. I.; Sutherland, R. G. *J. Organomet. Chem.* **1982**, *231*, 151.
(44) Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485.
(45) Bickert, P.; Hildebrant, B.; Hafner, K. *Organometallics* **1984**, *3*, 653.
(46) Arnold, R. T.; Danzig, M. J. *J. Am. Chem. Soc.* **1957**, *79*, 892.

Scheme IV



Scheme V



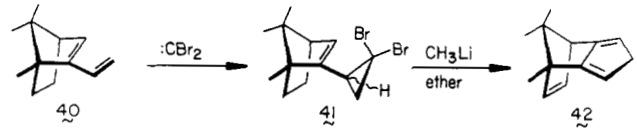
to obtain the two isomers in isomerically pure form by chromatography.

A quick glance at Table II reveals that the diamagnetic shielding experienced by the endo methyl or syn apical hydrogen is significantly less for ruthenium than for iron. This phenomenon is likely linked to the distance of the metal from the centroid of the proximal cyclopentadienide ring, which is approximately 0.15 Å greater for Ru than for Fe.[14b]

Discussion

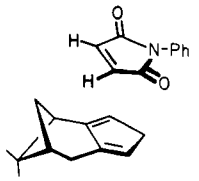
The ease of obtaining homochiral dienes such as **15** and **40**,[22] the regioselectivity with which they undergo dibromocarbene addition, and the high efficiency with which cyclopentadiene annulation occurs from both diastereomeric dibromocyclopropanes indicate the Skattebøl procedure to possess considerable practicality.

Where **3** is concerned, the collective Diels–Alder results show that [4 + 2] cycloaddition proceeds with a kinetic preference for bonding to that cyclopentadiene face which is syn to the less sterically congested methano bridge (i.e., **43**). The remarkably comparable data for *N*-phenyl-

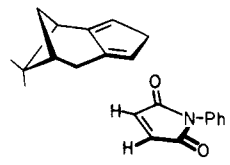


maleimide (10:1 or 91%) and *p*-benzoquinone (9:1 or 90%) reveal also that only anti-Alder alignment is involved in either approach trajectory. These features are illustrated in **43** and **44**. The nonbonded steric repulsions generated during incipient bonding as in **44** can be reasonably attributed to the cause of the 10-fold rate retardation.

Despite the rod-shaped nature of dimethyl acetylenedicarboxylate, the product ratio (6:1 = 86%) represents only a quite small diffrence from the cases just discussed. On the other hand, (*Z*)-1,2-bis(phenylsulfonyl)ethylene captures **3** only from the direction of its unsubstituted methano bridge. Another important distinction surfaces.



43



44

This dienophile exhibits a greater demand for capture in the Alder mode and actually delivers **24** as 30% of the product mixture. This feature may not have an electronic origin, but merely be the result of relatively longer C–S bonds such that the phenylsulfonyl groups are now projected further from the endo apical hydrogen.

Reaction of **3** and the anion of **3**, respectively, with $Fe(CO)_5$ and $TiCl_4$ likewise proceeds in stereochemically homogeneous fashion from the more open face. Comparable levels of stereocontrol do not accompany the ligand transfer reactions involving **29** and **35**, although the ruthenium example does sense a quite good kinetic driving force for complexation from the same direction. The stronger preference for Ru (7:93) relactive to Fe (27:73) for bonding to the less hindered face of a 4-(dimethylamino)-substituted fulvene has been noted previously[14b] and remains to be satisfactorily rationalized.

It is not coincidental that **3** uniformly undergoes Diels–Alder capture and metal complexation from the less hindered above-plane direction (as drawn). Steric effects brought on by the endo-methyl substituent are controlling. This behavior is strikingly different from that earlier established for the norbornyl- (**1**) and norbornenyl-fused (**2**) cyclopentadienes, which generally experience [4 + 2] bonding predominantly from below-plane[3-6] and metal complexation on their exo surface.[14] This contrast draws one inevitably to the conclusion that the effects which emanate from the laterally fused bicyclo[2.2.1]heptane subunits in **1** and **2** have considerable impact on the π-face stereochemical outcome of the Diels–Alder reactions.

Experimental Section

(1*R*)-(−)-Nopol Tosylate (14b). A mechanically stirred solution of (1*R*)-(−)-nopol (125 g, 0.752 mol) in 500 mL of pyridine was cooled to −10 °C in an ice–salt bath under nitrogen. *p*-Toluenesulfonyl chloride (175 g, 0.918 mol) was added in one portion under the inert atmosphere via Gooch tubing. The temperature rose to 40 °C during 15–20 min, but returned to 5 °C where it was maintained for 2 h. Twenty 1-mL portions of water were next introduced at such a rate that the temperature did not exceed 5 °C. The reaction mixture was poured into ether (1 L) and extracted with ice-cold 5 M sulfuric acid until the aqueous layer remained acidic. The ethereal phase was washed with two 200-mL portions each of water and 5% sodium bicarbonate solution prior to drying and solvent evaporation. The residual material was dissolved in hexane and filtered through a pad of Celite to remove a black-colored impurity. Finally, **14b** was recrystallized six times from 500 mL of hexane aliquots to give 173 g (72%) of colorless crystals, mp 51.0–51.8 °C (lit.[24,26] mp 49–50 °C); $[\alpha]^{25}_D$ −25.6° (*c* 1.0, C_2H_5OH).

(1*R*)-(+)-Nopadiene (15). A mechanically stirred, nitrogen-blanketed solution of **14b** (200 g, 0.624 mol) in dimethyl sulfoxide (1 L, freshly distilled from calcium hydride) was cooled briefly in a cold water bath and treated in one portion with freshly sublimed potassium *tert*-butoxide (69.0 g, 0.615 mol). The base serves as limiting reagent to offest isomerization of product diene. The temperature rose to approximately 45 °C and a brown color developed. As reaction proceeded, the color dissipated to a light yellow hue. After the initial exotherm subsided, the mixture was heated at 75 °C for 10 h, cooled to room temperature, and diluted with 800 mL of hexane. The lower layer, mostly dimethyl sulfoxide, was diluted with 1 L of water and extracted with two 100-mL portions of hexane. The combined hexane layers were washed with water (5 × 200 mL), dried over magnesium sulfate, and rotary evaporated at 40 Torr and 25 °C to leave a yellow oil. Distillation through a 5-in. Vigreux column gave 74.0 g (80%) of **15** as a clear colorless oil, bp 78–79 °C/25 Torr; $[\alpha]^{24}_D$ +3.8° (*c* 8.4, hexane).[47]

Dibromocarbene Addition to 15. A 250-mL flask was charged with 26.2 mL (0.30 mol) of bromoform, 29.6 g (0.20 mol) of **15**, 1.0 g (4.4 mmol) of benzyltriethylammonium chloride, 0.8 mL of ethanol, and 20 mL of dichloromethane. The suspension was stirred and cooled in an ice bath while 100 mL of 50% sodium hydroxide solution was added over 10 min from a dropping funnel. The reaction mixture was stirred at room temperature for 24 h and poured into 250 mL of water. The lower layer was separated and the aqueous phase was extracted with three 25-mL portions of dichloromethane. The combined organic layers were washed with three 100-mL portions of water, dried, and concentrated in vacuo to give a brown-black oil. The oil was dissolved in an equal volume of hexane and filtered through a 2-in. bed of silica gel with hexane (1.5 L) as eluant. The solvent was evaporated and the orange oil was distilled in an apparatus protected from light at 85–95 °C and 0.08 Torr. The yellow distillate was redistilled through a covered 4-in. Vigreux column to give 35.2 g (55%) of the diastereomeric dibromocyclopropanes **16**. The ^1H NMR spectrum was complex; however, the pair of olefinic multiplets at δ 5.48 and 5.33 (4:1 ratio) and the methyl singlets at δ 1.29 and 0.89 (in $CDCl_3$ solution) were particularly diagnostic.

(1*R*)-(−)-9,9-Dimethyltricyclo[6.1.1.0^{2,6}]deca-2,5-diene (3). A flame-dried 3-L flask was charged with 17.6 g (55.0 mmol) of **16** and a total of 2 L of anhydrous ether was introduced via cannula. The stirred solution was cooled in an ice bath and 147 mL of 1.5 M methyllithium in ether (220 mmol) was introduced via a second cannula. The ice bath was removed and stirring was maintained for 10 h before the solution was cannulated into 1 L of ice-cold water. The ether layer was separated and the aqueous phase was extracted with two 200-mL portions of ether. The combined ethereal solutions were dried and concentrated. The residual yellow oil was immediately diluted with an equal volume of hexane and passed through a short column of neutral alumina. The solvent was carefully removed and the yellow oil was subjected to bulb-to-bulb distillation at 90 °C and 5 Torr to give 7.7 g (87%) of **3** as a colorless oil: $[\alpha]^{23}_D$ −21.9° (*c* 1.76, C_2H_5OH); ^1H NMR (300 MHz, $CDCl_3$) δ 5.99 (s, 1 H), 5.77 (s, 1 H), 2.99 (s, 2 H), 2.70 (m, 2 H), 2.60 (m, 1 H), 2.11 (m, 1 H), 1.60 (s, 1 H), 1.33 (s, 3 H), 1.24 (m, 1 H), 0.72 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 152.5, 142.0, 125.3, 120.3, 44.1, 41.3, 40.9, 32.6, 28.5, 26.7, 26.5, 21.5; MS, *m/z* (M^+) calcd 160.1252, obsd 160.1237.

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.16. Found: C, 89.76; H, 10.09.

***N*,*N*-Dimethyl-1-(5,5-dimethyl-4,5,6,7-tetrahydro-4,6-methano-2*H*-inden-2-ylidene)methanamine (4).** Dimethyl sulfate (distilled from calcium oxide; 1.2 mL, 0.013 mol) was added dropwise to warm (50–60 °C), stirred dimethylformamide (distilled from calcium hydride; 1.0 mL, 0.013 mol) under a blanket of nitrogen. The solution was heated to 70–80 °C for 2.5 h and allowed to cool to room temperature. In a separate flask, *n*-butyllithium (9.2 mL, 1.37 M in hexane, 0.013 mol) was added to a cold (−78 °C), magnetically stirred solution of **3** (16 mL of 0.785 M in hexane, 0.013 mol) in dry tetrahydrofuran (10 mL). After 40 min of stirring, the solution was warmed to −10 °C and the dimethylformamide–dimethyl sulfate complex was introduced via cannula. Once addition was complete, the reaction mixture was slowly warmed to room temperture and stirred overnight.

The dark orange mixture was filtered and the residue was washed with tetrahydrofuran until the washings were colorless. Evaporation of the filtrate gave a dark orange oil. The oil was dissolved in *n*-heptane (200 mL), decolorized with charcoal, and filtered. The filtrate was concentrated to approximately 75 mL and set in a freezer. The precipitate was collected to provide 0.651 g (24%) of **4** as pale yellow plates, mp 119–120 °C (1:1 mixture of *E*/*Z* isomers): IR ($CHCl_3$, cm^{-1}) 2980, 2950, 2930, 2915, 2860, 2830, 2800, 1708, 1620, 1580, 1510, 1480, 1465, 1440, 1430, 1405,

(47) Nopol tosylate exhibiting $[\alpha]^{20}_D$ −29.7° (*c* 1.0, C_2H_5OH) has previously been reported to give nopadiene of ca. 100% ee with $[\alpha]^{20}_D$ 1.3° (*c* 1.5, $CHCl_3$). Samuel, O.; Couffigual, R.; Lauer, M.; Zhang, S. Y.; Kagan, H. B. *Nouv. J. Chem.* **1981**, 15.

1390, 1380, 1365, 1342, 1215, 1145, 1095, 1065, 1008, 945, 930, 808, 662, 625; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (s, 2 H), 6.29 (s, 1 H), 6.12 (d, J = 2 Hz, 1 H), 6.02 (s, 1 H), 5.88 (d, J = 2 Hz, 1 H), 3.16 (s, 12 H), 2.88 (s, 2 H), 2.83 (s, 2 H), 2.74 (q, J = 5 Hz, 2 H), 2.69–2.62 (m, 2 H), 2.19–2.14 (m, 2 H), 1.37 (s, 3 H), 1.36 (s, 3 H), 1.33 (d, J = 5 Hz, 2 H), 0.76 (s, 3 H), 0.75 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 149.07, 143.79, 143.50, 142.69, 136.91, 130.46, 119.45, 117.60, 117.55, 115.33, 109.85, 106.04, 44.29, 43.60, 42.83, 42.77, 41.87, 41.79, 41.34, 41.28, 33.67, 33.48, 28.97, 28.31, 26.75, 21.91; $[\alpha]^{23}_D$ −46.7° (c 0.36, $CHCl_3$); MS, m/z (M^+) calcd 215.1674, obsd 215.1678.

Anal. Calcd for $C_{15}H_{21}N$: C, 83.67; H, 9.83. Found: C, 83.41; H, 9.81.

Cycloaddition of 3 with *N*-Phenylmaleimide. *N*-Phenylmaleimide (324 mg, 2.0 mmol) ws added to a stirred solution of **3** (2.5 mL of 0.785 M in hexane, 2.0 mmol) in dry benzene (20 mL). Stirring was continued at room temperature under a blanket of nitrogen for 16 h. The solvent was removed to give a pale yellow residue consisting of **18** and **19** in a 1:9 ratio (300-MHz ^{1}H NMR analysis). The isomers were separated by MPLC on silica gel (elution with 20% ethyl acetate in petroleum ether); 44 mg (7.1%) of **18** and 259 mg (41.5%) of **19** were isolated as white, powdery solids. A small amount of uncharacterized material was also obtained (≲5%).

For **18**: mp 167–169 °C (from hexanes); IR ($CHCl_3$, cm^{-1}) 3025, 2985, 2935, 2875, 2825, 1765, 1698, 1595, 1498, 1465, 1455, 1375, 1265, 1215, 1180, 1130, 1080, 945, 870, 800, 689, 655, 615; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–7.25 (series of m, 5 H), 3.26 (s, 1 H), 3.24 (s, 1 H), 3.02 (d, J = 7 Hz, 1 H), 2.95 (d, J = 7 Hz, 1 H), 2.54–2.47 (m, 2 H), 2.38 (t, J = 5 Hz, 1 H), 2.25–2.15 (m, 2 H), 1.67 (d, J = 10 Hz, 1 H), 1.50 (d, J = 10 Hz, 1 H), 1.30 (s, 3 H), 1.24 (d, J = 9 Hz, 1 H), 0.61 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 177.48, 177.32, 154.11, 137.64, 131.97, 129.14, 128.58, 126.40. 49.26, 48.67, 48.56, 47.83, 43.69, 42.53, 41.47, 40.01, 33.44, 29.15, 26.60, 21.56; $[\alpha]^{23}_D$ −8.5° (c 0.46, $CHCl_3$); MS, m/z (M^+) calcd 333.1729, obsd 333.1740.

For **19**: mp 220–221 °C (from hexanes); IR ($CHCl_3$, cm^{-1}) 2980, 2930, 2875, 2820, 1765, 1700, 1595, 1500, 1465, 1455, 1420, 1375, 1285, 1280, 1270, 1260, 1215, 1180, 1130, 1080, 1060, 1030, 1020, 1005, 945, 920, 910, 890, 870, 690, 615; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–7.24 (series of m, 5 H), 3.26 (s, 1 H), 3.24 (s, 1 H), 2.96 (d, J = 7 Hz, 1 H), 2.83 (d, J = 7 Hz, 1 H), 2.51–2.43 (m, 2 H), 2.33 (t, J = 5 Hz, 1 H), 2.21–2.13 (m, 2 H), 1.65 (d, J = 10 Hz, 1 H), 1.48 (d, J = 10 Hz, 1 H), 1.30 (s, 3 H), 0.87 (s, 3 H), 0.68 (d, J = 9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 177.18, 177.00, 152.36, 138.33, 131.91, 129.07, 128.50, 126.36, 49.49, 49.31, 48.26, 41.6,, 41.51, 40.13, 33.48, 29.61, 26.50, 21.40; $[\alpha]^{23}_D$ −76.5° (c 0.31, $CHCl_3$); MS, m/z (M^+) calcd 333.1729, obsd 333.1742.

Anal. Calcd for $C_{22}H_{23}NO_2$: C, 79.25; H, 6.95. Found: C, 79.15; H, 7.06.

Cycloaddition of 3 with *p*-Benzoquinone. To a stirred deoxygenated solution of *p*-benzoquinone (198 mg, 1.8 mmol) in dry benzene (10 mL) was added **1** (2.5 mL of 0.785 M in hexane, 2.0 mmol) via syringe. The reaction flask was covered with foil and the reaction mixture was stirred at room temperature under nitrogen for 24 h. Removal of the solvent produced a bright yellow residue containing **20** and **21** in a ratio of 1:10 (300-MHz ^{1}H NMR analysis). The adducts were separated by MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether) to give 13.6 mg (2.8%) of **20** and 193.2 mg (40%) of **21** as a pale yellow solids, as well as a small amount of uncharacterized material (≲5%).

For **20**: mp 123.5–125 °C; IR ($CHCl_3$, cm^{-1}) 3020, 2990, 2935, 2870, 2835, 1660, 1610, 1465, 1380, 1360, 1270, 1215, 1130, 1105, 1025, 885, 850; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.74 (s, 2 H), 3.12 (s, 1 H), 3.09 (s, 1 H), 2.67 (d, J = 8 Hz, 1 H), 2.61 (d, J = 8 Hz, 1 H), 2.51–2.40 (m, 3 H), 2.23 (dd, J = 2, 18 Hz, 1 H), 2.15–2.11 (m, 1 H), 1.44 (d, J = 9 Hz, 1 H), 1.35 (d, J = 9 Hz, 1 H), 1.28 (s, 3 H), 1.22 (d, J = 9 Hz, 1 H), 0.54 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 199.73, 199.51, 153.85, 141.73, 141.69, 137.20, 52.87, 51.44, 49.45, 49.08, 45.66, 42.56, 41.53, 40.09, 33.53, 29.04, 26.66, 21.41; $[\alpha]^{23}_{546}$ +3.6° (c 0.22, $CHCl_3$); MS, m/z (M^+) calcd 268.1463, obsd 268.1453.

For **21**: mp 169–170 °C; IR ($CHCl_3$, cm^{-1}) 3020, 2980, 2930, 2870, 2820, 1660, 1605, 1475, 1460, 1380, 1365, 1270, 1215, 1140, 1130, 1105, 1025, 960, 895, 855; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.74 (s, 2 H), 3.13 (s, 1 H), 3.10 (s, 1 H), 2.62 (d, J = 8 Hz, 1 H), 2.51–2.35 (series of m, 4 H), 2.21 (dd, J = 3, 18 Hz, 1 H), 2.16–2.11 (m, 1 H), 1.43 (d, J = 9 Hz, 1 H), 1.34–1.30 (overlapping d and s, 4 H), 0.86 (s, 3 H), 0.62 (d, J = 9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 199.50, 199.26, 151.66, 141.79, 138.14, 52.98, 52.09, 50.30, 49.20, 43.31, 41.80, 41.58, 40.25, 33.38, 29.53, 26.58, 21.41; $[\alpha]^{23}_D$ −70.5° (c 0.54, $CHCl_3$); MS, m/z (M^+) calcd 268.1463, obsd 268.1453.

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.33; H, 7.53.

Cycloaddition of 3 with Dimethyl Acetylenedicarboxylate. To a stirred, deoxygenated solution of **3** (2.5 mL of 0.785 M in hexane, 2.0 mmol) in dry benzene (10 L) was added dimethyl acetylenedicarboxylate (0.25 mL, 2.0 mmol) via syringe. The solution was stirred under nitrogen at room temperature for 48 h. Evaporation of the solvent afforded a yellow oil shown to be a 1:6 mixture of **22** and **23** (300-MHz ^{1}H NMR analysis). The cycloadducts were separated by MPLC on silica gel (elution with 5% ethyl acetate in petroleum ether) to give 0.129 g (21.4%) of **22** and 0.407 g (67.3%) of **23**.

For **22**: IR ($CHCl_3$, cm^{-1}) 3025, 2990, 2950, 2940, 2875, 2830, 1720, 1705, 1615, 1465, 1430, 1380, 1365, 1315, 1260, 1240, 1195, 1120, 1105, 1050, 1020; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.80 (s, 3 H), 3.75 (s, 4 H), 3.65 (d, J = 2 Hz, 1 H), 2.59 (dd, J = 3, 18 Hz, 1 H), 2.52–2.34 (series of m, 3 H), 2.25 (dd, J = 2, 18 Hz, 1 H), 2.16–2.09 (m, 2 H), 1.28 (d, J = 8 Hz, 1 H), 1.25 (s, 3 H), 0.41 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 166.35, 165.61, 158.18, 153.60, 151.04, 142.97, 71.66, 56.20, 54.99, 51.95, 51.84, 43.29, 41.99, 40.86, 33.63, 31.18, 26.55, 21.38; $[\alpha]^{23}_D$ +37.7° (c 0.85, $CHCl_3$); MS, m/z (M^+) calcd 302.1518, obsd 302.1515.

For **23**: IR ($CHCl_3$, cm^{-1}) 3020, 2985, 2945, 2940, 2885, 2870, 2830, 1725, 1705, 1615, 1430, 1310, 1260, 1240, 1190, 1125, 1105, 1050, 1020, 910; ^{1}H NMR (300 MHz, $CHCl_3$) δ 3.75 (s, 6 H), 3.71 (d, J = 1.4 Hz, 1 H), 3.64 (d, J = 1.2 Hz, 1 H), 2.57 (dd, J = 3, 18 Hz, 1 H), 2.43–2.16 (series of m, 5 H), 2.10–2.04 (m, 1 H), 1.25 (s, 3 H), 0.86 (s, 3 H), 0.67 (d, J = 9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 165.96, 165.90, 157.75, 153.18, 152.26, 142.93, 69.88, 55.79, 55.15, 51.85, 51.82, 43.18, 41.42, 40.41, 33.04, 31.61, 26.42, 21.41; $[\alpha]^{23}_D$ −51.4° (c 1.4, $CHCl_3$); MS, m/z (M^+) calcd 302.1518, obsd 302.1507.

Cycloaddition of 3 with (*Z*)-1,2-Bis(phenylsulfonyl)-ethylene. A solution of **3** (0.7 mL of 0.785 M in hexane, 0.5 mmol) and the disulfone (158 mg, 0.5 mmol) in dry benzene (10 mL) was heated at 45 °C under an atmosphere of nitrogen for 24 h. During this time a white precipitate formed. The reaction mixture was concentrated to leave a residue consisting of **24** and **25** in a ratio of 1:2.2 (300-MHz ^{1}H NMR analysis). Recrystallization of this mixture from ethyl acetate–hexane provided pure **25**. The mother liquor was concentrated and subjected to radial chromatography (silica gel, elution with 30% ethyl acetate in petroleum ether) to give **24** and additional **25**.

For **24**: 25 mg (10.4%); colorless crystals, mp 221 °C dec (from ethyl acetate–hexane); IR ($CHCl_3$, cm^{-1}) 3050, 3020, 2980, 2930, 2870, 2830, 1445, 1340, 1330, 1260, 1150, 1085, 690, 650, 610; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05–7.51 (series of m, 10 H), 4.22 (dd, J = 3, 10 Hz, 1 H), 4.07 (dd, J = 3, 10 Hz, 1 H), 3.20 (s, 1 H), 3.01–2.95 (overlapping dd and s, 2 H), 2.59–2.54 (m, 1 H), 2.48 (t, J = 5 Hz, 1 H), 2.41 (dd, J = 3, 17 Hz, 1 H), 2.23–2.17 (m, 2 H), 1.77 (d, J = 9 Hz, 1 H), 1.38 (s, 3 H), 1.30 (d, J = 9 Hz, 1 H), 0.82 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 150.06, 141.87, 137.67, 133.30, 133.24, 128.91, 128.81, 12,974, 128.60, 71.31, 70.86, 50.58, 58.08, 43.58, 41.66, 40.01, 31.79, 31.03, 26.70, 21.55; $[\alpha]^{23}_D$ −42.5° (c 0.18, $CHCl_3$); MS, m/z (M^+) calcd 468.1429, obsd 468.1417.

For **25**: 118 mg (49.1%); colorless solid, mp 204–205 °C (from ethyl acetate–hexane); IR ($CHCl_3$, cm^{-1}) 3060, 3020, 2980, 2930, 2880, 2820, 1445, 1340, 1330, 1310, 1165, 1150, 1090, 1080, 690, 650; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02–7.67 (series of m, 10 H), 3.49 (dd, J = 2, 9 Hz, 1 H), 3.36 (dd, J = 2, 9 Hz, 1 H), 3.07 (s, 1 H), 3.04 (s, 1 H), 2.57 (dt, J = 2, 10 Hz, 1 H), 2.43–2.36 (m, 1 H), 2.26 (dd, J = 2, 18 Hz, 1 H), 2.06–2.01 (m, 1 H), 1.97 (t, J = 5 Hz, 1 H), 1.79 (dd, J = 3, 18 Hz, 1 H), 1.61 (d, J = 10 Hz, 1 H), 1.20 (s, 3 H), 0.73 (s, 3 H), 0.50 (d, J = 9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 153.14, 141.09, 141.02, 139.31, 133.46, 128.95, 128.91, 128.87, 128.66, 69.30, 68.72, 50.38, 49.04, 44.05, 41.54, 41.26, 40.42, 33.75, 29.42, 26.34, 21.29; $[\alpha]^{23}_D$ −40.4° (c 0.54, $CHCl_3$); MS, m/z (M^+) calcd 468.1429, obsd 468.1458.

Anal. Calcd for $C_{26}H_{28}O_4S_2$: C, 66.64; H, 6.02. Found: C, 66.66; H, 6.19.

Reductive Desulfonylation of 25. Sodium amalgam (1.5% w/w, 1.45 g) was added in portions to a suspension of **25** (52.3 mg, 0.11 mmol) and sodium dihydrogen phosphate (300 mg) in anhydrous methanol (5 mL). The slurry was vigorously stirred under a nitrogen atmosphere for 3 h. The mercury was removed and water (25 mL) was added. The mixture was transferred to a separatory funnel and extracted with dichloromethane (2 × 10 mL). The organic layer was dried, decanted, and carefully concentrated on a rotary evaporator. The resulting oil was passed through a small pipet column of silica gel (elution with pentane). Evaporation of the solvent gave 10.5 mg (50%) of hydrocarbon **26** as a colorless liquid: IR (neat, cm^{-1}) 3110, 3060, 2965, 2925, 2860, 2820, 1550, 1465, 1445, 1425, 1380, 1360, 1285, 1255, 1220, 1190, 1095, 1075, 1055, 1015, 890, 860, 805, 775, 720, 685, 670, 645; ^1H NMR (300 MHz, $CDCl_3$) δ 6.81 (dd, J = 3.0, 5.0 Hz, 1 H), 6.71 (dd, J = 3.0, 5.0 Hz, 1 H), 3.32 (br s, 1 H), 3.26 (br s, 1 H), 2.55 (dd, J = 3.0, 17.8 Hz, 1 H), 2.33–2.29 (m, 2 H), 2.09–1.98 (m, 4 H), 1.29 (s, 3 H), 0.89 (s, 3 H), 0.68–0.63 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 156.97, 143.18, 142.46, 141.89, 72.10, 52.59, 51.67, 43.41, 41.62, 40.64, 32.92, 32.14, 26.68, 21.51; MS, m/z (M^+) calcd 186.1409, obsd 186.1393.

Reductive Desulfonylation of 24. The sodium amalgam mediated desulfonylation of **24** (43.6 mg, 0.08 mmol) was performed as described above by using 1.21 g of 1.5% amalgam in phosphate-buffered methanol (5 mL) to give 6.2 mg (36%) of diend **26** identical with that obtained from **25** by ^1H NMR analysis.

Reaction of 3 with Iron Pentacarbonyl. A 250 mL, three-necked flask was equipped with a magnetic stirring bar, reflux condenser, and Schlenk filter tube that was attached to another sealed 250 mL three-necked flask fitted with an argon inlet and serum stoppers. The apparatus was flame-dried and charged in turn with 80 mL of isooctane, 16.5 g (0.175 mol) of norbornene, and 7.28 g (45.4 mmol) of **3**. Stirring was begun, the solution was cooled to −78 °C, and iron pentacarbonyl (21 mL, 0.160 mol) was introduced. The mixture was immediately deoxygenated via four successive pump, purge, thaw, and freeze cycles involving argon. The yellowish mixture was heated at the reflux temperature for 40 h and suction-filtered while hot. The violet filtrate on cooling to room temperature deposited spectroscopically pure **27** (60%). Cooling of the mother liquor to −14 °C and removal of the solvent via cannulation gave an additional 10% of product. The total yield of **27** was 8.30 g: purple brown crystals, mp 178 °C dec; IR (KBr, cm^{-1}) 2938, 1965, 1765, 1451, 1385, 1365, 871, 820; ^1H NMR (300 MHz, CD_3COCD_3) δ 4.72 (s, 2 H), 4.42 (s, 2 H), 3.85 (s, 2 H), 3.06 (dd, J = 2.8, 16.4 Hz, 2 H), 2980 (m, 4 H), 2.59 (t, J = 5.4 Hz, 2 H), 2.44 (dd, J = 2.5, 16.4 Hz, 2 H), 2.27 (m, 2 H), 1.42 (s, 6 H), 0.68 (s, 6 H); ^{13}C NMR (75 MHz, CD_2Cl_2, 0.01 M $Cr(acac)_3$) ppm 117.4, 102.8, 90.0, 81.5, 81.3, 42.0, 41.6, 41.2, 37.8, 26.8, 24.8, 21.6 (carbonyls not observed); MS, m/z (M^+) calcd 542.0842, obsd 542.0799.

Anal. Calcd for $C_{28}H_{30}Fe_2O_4$: C, 62.02; H, 5.58. Found: C, 61.73; H, 5.63.

Dichlorobis(9,9-dimethyltricyclo[6.1.1.0^{2,6}]deca-2,5-dienyl)titanium (28). A 150-mL Schlenk tube equipped with filtration tube and argon inlet was charged with 2.00 g (12.5 mmol) of **3** and 30 mL of anhydrous ether. The solution was stirred at 0 °C while 12.2 mmol of *n*-butyllithium in hexane was slowly added. A yellow solid precipitated. After 15 min, 0.68 mL (6.20 mmol) of titanium tetrachloride was gradually introduced. The solution turned dark red and a dark-colored precipitate formed. The mixture was shaken frequently and allowed to warm to room temperature. After 30 min, the ether was removed in vacuo and the red-brown residue was triturated with dichloromethane (75 mL) and filtered. The filtrate was concentrated to a volume of 20 mL and hexane (100 mL) was added. The dark red solution was cannulated away from 0.45 g of red microcrystals. The concentrated mother liquor was triturated with hexane to leave an additional 0.60 g of **28** (total yield 38.5%), mp 240 °C dec (from 1:2 dichloromethane–hexane): IR (KBr, cm^{-1}) 2944, 2922, 2860, 1473, 1424, 1381, 1369, 820; ^1H NMR (300 MHz, $CDCl_3$) δ 6.13 (m, 4 H), 5.95 (m, 2 H), 3.39 (dd, J = 2.7, 17.3 Hz, 2 H), 2.79 (m, 2 H), 2.44 (m, 2 H), 2.09 (m, 2 H), 1.36 (s, 6 H), 1.12 (d, J = 9.8 Hz, 2 H), 0.49 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 140.5, 138.7, 120.8, 115.5, 111.8, 43.8, 42.3, 40.5, 31.4, 29.1, 26.1, 21.2; $[\alpha]^{23}_D$ +1240° (*c* 0.26, toluene); MS, m/z (M^+ − Cl) calcd 401.1518, obsd 401.1517.

Anal. Calcd for $C_{24}H_{30}Cl_2Ti$: C, 65.92; H, 6.91. Found: C, 65.88; H, 6.86.

(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,3a,7a-η)-5,5-dimethyl-2-formyl-4,5,6,7-tetrahydro-4,6-methano-2*H*-inden-1-yl]iron (30 and 31). A deoxygenated solution of **4** (99.7 mg, 0.46 mmol) and **29** (211.7 mg, 0.57 mmol) in dry dichloromethane (25 mL) was irradiated with a 250-W sunlamp for 24 h while being stirred under nitrogen. After the red solution cooled to room temperature, 2 N sodium hydroxide (10 mL) and ethanol (10 mL) were added. The mixture was stirred for 1.5 h, diluted with water (50 mL), and extracted into dichloromethane (2 × 50 mL). The combined organic extracts were washed with brine (1 × 50 mL), dried, filtered, and concentrated to yield a red-orange oil. MPLC purification on silica gel (elution with 10% ethyl acetate in petroleum ether) afforded 123 mg (86%) of a 27:73 mixture of aldehydes **30** and **31**. The key signals used for integration were the methyl signals (in $CDCl_3$) due to **30** (δ 1.44, 1.36) and **31** (δ 1.35, 0.47).

(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,3a,7a-η)-5,5-dimethyl-4,5,6,7-tetrahydro-2-(hydroxymethyl)-4,6-methano-2*H*-inden-1-yl]iron (32 and 33). A solution of the **30**/**31** mixture (173 mg, 0.6 mmol) in 95% ethanol (25 mL) was treated with sodium borohydride (35 mg, 0.9 mmol) and stirred at room temperature under nitrogen for 45 min. Water (50 mL) was added and the reaction mixture was extracted into ether (3 × 50 mL). The combined ether layers were dried, filtered, and concentrated to leave a yellow-orange solid. The alcohols were separated by MPLC on silica gel (elution with 20% ethyl acetate in petroleum ether).

For **32**: 50.7 mg (27%); dark orange solid, mp 84–86 °C; IR (CCl_4, cm^{-1}) 3620, 3460, 3100, 2990, 2920, 2870, 1740, 1470, 1410, 1370, 1300, 1240, 1120, 1105, 1045, 1000, 940, 845, 705, 690, 670; ^1H NMR (300 MHz, C_6D_6) δ 4.23 (s, 2 H), 3.96 (s, 5 H), 3.90 (s, 1 H), 3.73 (s, 1 H), 2.60 (d, J = 16 Hz, 1 H), 2.35–2.19 (m, 3 H), 1.92 (m, 1 H), 1.54 (s, 3 H), 1.24 (s, 3 H), 1.03 (s, 1 H), 0.73 (d, J = 8 Hz, 1 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 98.50, 84.48, 81.40, 70.35, 69.80, 65.30, 61.80, 42.22, 41.44, 40.91, 36.28, 27.93, 27.23, 23.19; $[\alpha]^{23}_D$ +280.5 (*c* 0.69, CCl_4); MS, m/z (M^+) calcd 310.1020, obsd 310.1027.

For **33**: 87.8 mg (48%); light yellow solid. The analytical sample was obtained by sublimation [100 °C; 0.5 Torr]: mp 128.5–129.5 °C; IR (CCl_4, cm^{-1}) 3620, 3570, 3090, 2985, 2920, 2880, 1460, 1445, 1410, 1380, 1365, 1250, 1105, 1020, 1000, 935; ^1H NMR (300 MHz, C_6D_6) δ 4.21 (s, 1 H), 4.19 (s, 1 H), 3.93 (s, 6 H), 3.88 (s, 1 H), 2.59–2.57 (m, 2H), 2.31–2.24 (m, 3 H), 2.00–1.95 (m, 1 H), 1.24 (s, 3 H), 1.06 (m, 1 H), 0.53 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 98.35, 85.30, 82.12, 69.79, 65.00, 63.98, 61.25, 42.18, 41.84, 41.34, 35.92, 27.75, 26.94, 21.52; $[\alpha]^{23}_D$ −338.7° (*c* 0.39, CCl_4); MS, m/z (M^+) calcd 310.1020, obsd 310.1022.

Anal. Calcd for $C_{18}H_{22}FeO$: C, 69.69; H, 7.15. Found: C, 69.59; H, 7.15.

Oxidation of 32. A deoxygenated suspension of **32** (26 mg, 0.085 mmol) and active manganese dioxide (30 mg, 0.339 mmol) in dry benzene (6 mL) was stirred at room temperature under a nitrogen atmosphere for 26 h. After filtration and concentration, the orange residue was purified by chromatography on neutral alumina (elution with 20% ethyl acetate in petroleum ether) to give 16 mg (62%) of pure **30** as a thick, orange oil: IR (CCl_4, cm^{-1}) 3100, 3000, 2930, 2750, 1730, 1680, 1475, 1460, 1388, 1370, 1115, 1010, 950, 845, 830, 720; ^1H NMR (300 MHz, C_6D_6) δ 9.97 (s, 1 H), 4.43 (s, 1 H), 4.28 (s, 12 H), 3.95 (s, 5 H), 2.47 (dd, J = 2, 16 Hz, 1 H), 2.30 (d, J = 9 Hz, 1 H), 2.23 (t, J = 5 Hz, 1 H), 2.14 (dd, J = 2, 16 Hz, 1 H), 1.86–1.82 (7, 1 H), 1.26 (s, 3 H), 1.16 (s, 3 H), 0.60 (d, J = 9 Hz, 1 H); $[\alpha]^{23}_D$ +295.8° (*c* 0.22, CCl_4); MS, m/z (M^+) calcd 308.0863, obsd 308.0861.

Oxidation of 33. A deoxygenated mixture of **33** (14 mg, 0.045 mmol) in dry benzene (6 mL) containing active manganese dioxide (16 mg, 0.181 mmol) was stirred at room temperature under nitrogen for 23 h. The suspension was filtered through Celite and the filtrate was concentrated to leave a dark orange solid. MPLC on silica gel (elution with 10% ethyl acetate in petroleum ether) provided 13 mg (94%) of pure **31** as an orange powder, mp 89–91 °C: IR (CCl_4, cm^{-1}) 3090, 3000, 2980, 2930, 2870, 2740, 1675, 1460, 1410, 1385, 1370, 1110, 1105, 1000, 840; ^1H NMR (300 MHz, C_6D_6) δ 9.92 (s, 1 H), 4.42 (s, 1 H), 4.39 (s, 1 H), 3.91 (s, 5 H), 2.51–2.45

(m, 2 H), 2.26–2.19 (m, 2 H), 1.88–1.85 (m, 1 H), 1.86 (d, J = 9 Hz, 1 H), 1.18 (s, 3 H), 0.43 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 193.19, 103.09, 87.07, 76.66, 70.63, 66.29, 65.49, 41.74, 41.22, 35.43, 27.57, 26.70, 21.32; $[\alpha]^{23}_D$ −420.3° (c 0.25, CCl_4); MS, m/z (M^+) calcd 308.0863, obsd 308.0865.

Dehydrative Coupling of 33. A deoxygenated solution of **33** (20 mg, 0.065 mmol), p-toluenesulfonyl chloride (6.2 mg, 0.032 mmol), and triethylamine (4 drops) in dry benzene (20 mL) was stirred at room temperature under nitrogen for 44 h. Water was added and the product was extracted into ethyl acetate (3 × 30 mL). The combined organic extracts were dried, filtered, and concentrated. The yellow solid was purified by chromatography on silica gel (elution with 20% ethyl acetate in petroleum ether) to afford 19 mg (46%) of **34** as a yellow-orange solid, mp 160.5–162 °C (from hexanes): IR (CCl_4, cm^{-1}) 3100, 2980, 2930, 2865, 1740, 1465, 1445, 1370, 1240, 1105, 1045, 1000, 938, 845; ^{1}H NMR (300 MHz, C_6D_6) δ 4.33 (s, 2 H), 4.32 (s, 2 H), 4.09 (s, 2 H), 4.06 (s, 2 H), 4.02 (s, 10 H), 2.66 (dd, J = 3, 16 Hz, 2 H), 2.62–2.57 (m, 2 H), 2.34–2.28 (m, 4 H), 1.99–1.95 (m, 2 H), 1.24 (s, 6 H), 0.87 (t, J = 7 Hz, 2 H), 0.55 (s, 6 H); $[\alpha]^{23}_D$ −351.1° (c 0.24, CCl_4); MS, m/z (M^+) calcd 602.1934, obsd 602.1895.

(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,3a,7a-η)-5,5-dimethyl-2-formyl-4,5,6,7-tetrahydro-4,6-methano-2*H*-inden-1-yl]ruthenium (36 and 37). A solution of **4** (102 mg, 0.472 mmol) and **35** (184 mg, 0.424 mmol) in 1,2-dichloroethane (40 mL) was heated to reflux under a blanket of nitrogen for 24 h. After being cooled to room temperature, 2 N sodium hydroxide (15 mL) and ethanol (15 mL) were added and the mixture was stirred for 90 min, diluted with water (100 mL), extracted into dichloromethane (2 × 100 mL), dried, filtered, and concentrated. Purification by chromatography on silica gel (elution with 10% ethyl acetate in petroleum ether) provided a 7:93 mixture of **36** and **37** as a dark brown, viscous oil, 139 mg (93%). The key signals used for integration were the methyl signals (in C_6D_6) due to **36** (δ 1.14, 1.05) and **37** (δ 1.20, 0.62).

(η^5-2,4-Cyclopentadien-1-yl)[(1,2,3,3a,7a-η)-5,5-dimethyl-4,5,6,7-tetrahydro-2-(hydroxymethyl)-4,6-methano-2*H*-inden-1-yl]ruthenium (38 and 39). A solution of the **36/37** mixture (85.4 mg, 0.242 mmol) in 95% ethanol (25 mL) was treated with sodium borohydride (15 mg, 0.386 mmol) and stirred at room temperature under nitrogen for 45 min. Water (50 mL) was added and the product was extracted into ether (3 × 50 mL). The combined ethereal extracts were dried, filtered, and concentrated to leave a pale yellow solid. The alcohols were separated by MPLC on silica gel (elution with 20% ethyl acetate in petroleum ether).

For **38**: 4.8 mg (6%); dark tan solid, mp 90–92 °C; IR (CCl_4, cm^{-1}) 3525, 3460, 3100, 2980, 2930, 2865, 2080, 1880, 1730, 1475, 1460, 1440, 1390, 1370, 1355, 1295, 1235, 1095, 1040, 995, 935, 915, 845, 630, 600; ^{1}H NMR (300 MHz, C_6D_6) δ 4.46 (s, 1 H), 4.38 (s, 5 H), 4.31 (s, 1 H), 4.02 (s, 2 H), 2.54 (dd, J = 2, 16 Hz, 1 H), 2.47–2.42 (m, 2 H), 2.36 (dd, J = 4, 16 Hz, 1 H), 2.30 (t, J = 5 Hz, 1 H), 1.93–1.912 (m, 1 H), 1.25 (s, 3 H), 1.19 (s, 3 H), 0.99 (d, J = 9 Hz, 1 H); $[\alpha]^{23}_D$ +130.5° (c 0.19, CCl_4).

For **39**: 62 mg (72%); off-white powder. The analytical sample was obtained by sublimation [95 °C, 0.5 Torr]: mp 123–124 °C; IR (CCl_4, cm^{-1}) 3620, 3500, 3080, 2965, 2920, 2880, 1460, 1410, 1380, 1360, 1258, 1098, 10250, 995; ^{1}H NMR (300 MHz, C_6D_6) δ 4.54 (s, 1 H), 4.47 (s, 1 H), 4.38 (s, 5 H), 3.99 (d, J = 5 Hz, 2 H), 2.55 (dd, J = 3, 16 Hz, 1 H), 2.48 (d, J = 9 Hz, 1 H), 2.40 (dd, J = 3, 16 Hz, 1 H), 2.23 (t, J = 5 Hz, 1 H), 1.97–1.92 (m, 1 H), 1.81 (d, J = 9 Hz, 1 H), 1.25 (s, 3 H), 1.00 (t, J = 5 Hz, 1 H), 0.70 (s, 3 H); ^{13}C NMR (75 MHz, C_6D_6) ppm 103.30, 93.17, 86.32, 71.71, 69.43, 67.67, 59.30, 42.53, 41.28, 37.61, 27.75, 27.12, 21.90; $[\alpha]^{23}_D$ −186.6° (c 1.1, CCl_4); MS, m/z (M^+) calcd 356.0708, obsd 356.0738.

Anal. Calcd for $C_{18}H_{22}ORu$: C, 60.83; H, 6.24. Found: C, 60.85; H, 6.32.

Acknowledgment. We thank the National Institutes of Health for support of this research program through Grant CA-122115.

Physico-Chemical Studies of Doubly and Triply Unsaturated *syn*- and *anti*-Sesquinorbornanes. Photoelectron Spectroscopy, Molecular Orbital Calculations, and Deuterium-Induced ^{13}C NMR Shifts

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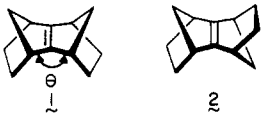
Received February 18, 1987

The photoelectron spectra of the *syn*- and *anti*-sesquinorbornadienes and -trienes **3–6** have been measured and compared to those recorded for the parent olefins **1** and **2**. These data have been analyzed with the aid of STO-3G and extended Hückel molecular orbital calculations. Deuterium-induced NMR shifts of ^{13}C resonance frequencies have been measured for the C-2 deuterium-labeled substrates **9**, **10**, and **13**. Various components of these three studies have provided diagnostic information concerning the bending about the central π bond that materializes in the syn series, although it has not been possible to gauge with any accuracy the magnitude of the deformation angle θ.

syn-Sesquinorbornene (**1**) has attracted the attention of many chemists due to its molecular structure and its reactivity. Several X-ray studies on **1** and its derivatives[3-5] reveal that the central double bond deviates by 12–22° from planarity. In contrast, most[3,4] though not all[6-8] *anti*-sesquinorbornenes (e.g., **2**) possess an essentially planar double bond. The bending observed in **1** has been rationalized in terms of (a) a diminished destabilizing in-



1 **2**

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