structure are obscured. Few data above 2θ = 40° were usable. The limited data set available was, however, sufficient to determine the gross overall structure and important nonbonded contacts.

Acknowledgment. The Ohio State group thanks the National Cancer Institute (Grant CA-12115) for their financial support of this research program.

Supplementary Material Available: Tables of final fractional coordinates, least-squares planes, and thermal parameters for **6**, **9**, **12**, and **14** (18 pages); listings of observed and calculated factors for **6**, **9**, **12**, and **14** (36 pages). Ordering information is given on any current masthead page.

Stereochemically Uniform Mode of Iron Carbonyl Complexation to Spirocyclic Isodicyclopentadienes[1]

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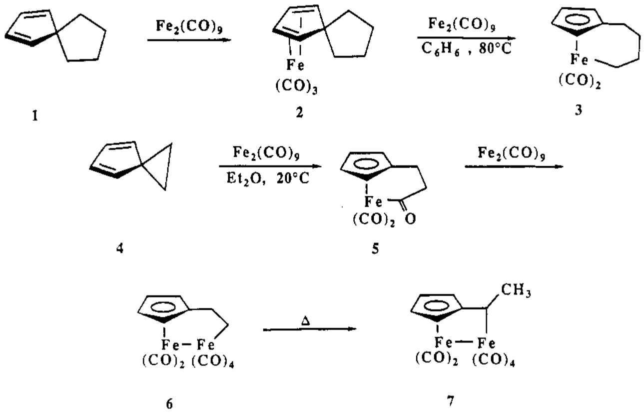
The ligands **14** and **15** derived by suitable spiroalkylation of isodicyclopentadiene were reacted with various iron carbonyl reagents in order to assess π-facial stereoselectivity and other reactivity differences. In contrast to the behavior of these dienes in Diels–Alder reactions, complexation occurred only above-plane. The less strained spiro[4.4]nonadiene **15** reacts with $Fe_2(CO)_9$ to form the η^4-complex **16**, the three-dimensional features of which were established by crystallographic analysis. The results of heating **15** with (BDA)$Fe(CO)_3$ in benzene were bond fission and formation of the σ-allyl π-isodicyclopentadienyl complex **17**. The latter substance could not be made to undergo carbonyl insertion. For **14**, heating with (BDA)$Fe(CO)_3$ led directly to the σ-acyl system **20** for which X-ray data were also obtained. Use of $Fe_2(CO)_9$ delivered a mixture of **20** and the fulvene complex **21**. The uniform mode of iron carbonyl complexation throughout this series is attributed to steric approach control.

The reactivity of 5,5-dialkyl-substituted cyclopentadienes toward various metal carbonyl reagents has been the subject of intense investigation,[3-9] particularly in recent times at the hands of Eilbracht and co-workers.[10] Notably prevalent in the resulting reactions is migration of an alkyl group from the five-membered ring to the metal so as to permit the establishment of (η^5-cyclopentadienyl)metal coordination. Spiro[4.4]nona-1,3-diene (**1**) and spiro[2.4]hepta-4,6-diene (**4**) have served as interesting substrates for study. Heating **1** with iron enneacarbonyl in benzene rapidly provides **2** and more slowly results in conversion predominantly to **3**.[10a,c,f,h,g,l] With $Fe_2(CO)_9$ in ether at 20 °C, **4** has been successfully transformed into the σ-acyl π-cyclopentadienyl complex **5**. At higher temperatures, the dinuclear complexes **6** and **7** are generated in turn.



Such C–C bond cleavage reactions also operate in monocyclic systems typified by **8**. In these examples, the availability of stereoisomeric complexes represented by **9** has permitted crossover experiments to be undertaken. The stereochemical results, e.g., **9** → **10**, have provided

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[1] Part 48 in the series dealing with isodicyclopentadienes and related molecules. (a) For part 47, see: Paquette, L. A.; Shen, C.-C.; Krause, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2351. (b) For part 46, see: Moriarty, K. J.; Rogers, R. D.; Paquette, L. A. *Organometallics* **1989**, *8*, 1512.

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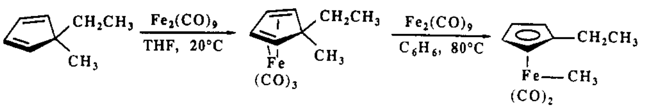
convincing evidence that the metal insertion process proceeds intramolecularly with migration of the endo alkyl group.[10c,f]



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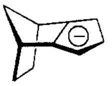
For some time now, we have recognized that isodicyclopentadiene enters into Diels–Alder reaction with a strong kinetic preference for below-plane dienophile capture, as long as untoward steric effects are kept to a minimum.[11] The derived anion 11 likewise captures electrophiles predominantly from the same direction at C-4.[12] In contrast, reaction of 11 with $Fe^{II}(acac)_2(py)_2$, $RuCl_3$, $OsCl_4$,[13] and related metal salts[14] has been shown to provide the corresponding metallocenes in which complexation has occurred exo (i.e., above-plane) to both ligands. Evidently, steric factors contribute heavily in dictating the stereochemical course of these reactions, since utilization of the endo π surface by either ligand would be accompanied by a considerable buildup of strain energy.



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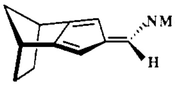

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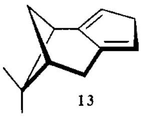


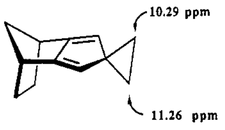
13

In an effort to remove at least some of this steric bias, the 4-methylisodicyclopentadienide anion and 4-(dimethylamino)isodicyclopentafulvene (**12**) have been complexed to group 6 transition-metal carbonyls.[15] While chromium exhibited the lowest above-plane coordinative ability (53%) toward the anion, tungsten showed the greatest (89%). Exclusive exo complexation was seen when fulvene **12** was condensed with the same triad of metal hexacarbonyls. More recently, stereocontrolled bifacial complexaton of **11** to cyclopentadienyltitanium fragments has been realized.[16] Under kinetically controlled conditions, endo complexation materializes at −78 °C; at room temperature and above, exo coordination operates exclusively. This striking dichotomy in reaction channel has spawned more recent investigations into the stereoselectivity with which **13** and optically active derivatives of **11** bind to titanium and zirconium.[17] A long-range goal is to develop uses for these compelxes in asymmetric synthesis.

Table I. Crystal and Data Collection Parameters for 16 and 20

	16	20
formula	$C_{17}H_{18}FeO_3$	$C_{15}H_{14}FeO_3$
cryst system	triclinic	orthorhombic
space group	$P\bar{1}$	*Pbca*
a, Å	8.725 (2)	12.523 (6)
b, Å	9.677 (3)	13.179 (7)
c, Å	10.012 (4)	16.114 (7)
α, deg	90.85 (3)	
β, deg	90.88 (3)	
γ, deg	114.71 (3)	
V, Å^3	767.6 (4)	2659.5
Z	2	8
D(calc), g cm^{-3}	1.41	1.49
μ, cm^{-1}	10.2	10.7
temp, °C	23	20
diffractometer	Nicolet R3m/μ	Enraf-Nonius CAD-4
radiatn	graphite-monochromated Mo Kα (λ = 0.71073 Å)	
cryst dimens, mm	0.21 × 0.25 × 0.27	0.25 × 0.32 × 0.40
scan speed, deg min^{-1}	variable, 6–20	variable, 6–20
2θ scan range, deg	$4 \le 2\theta \le 48$	$2 \le 2\theta \le 50$
scan technique	Wyckoff	$\theta/2\theta$
data collected	2553	2670
indpndt data	2397	2670
indpndt data with $F_o \le 5\sigma(F_o)$	2047	1033
R(int), %	4.21	
std rflns	3 stds/197 rflns (var < 1%)	3 stds/3600 rflns (var < 2%)
$R(F)$, %	3.93	4.8
$R(wF)$, %	4.30	4.8
Δ/σ (final max)	0.103	<0.01
data/parameter ratio	7.9	6.0
GOF	1.277	0.91

In the present study, we have sought to gain appreciation of the manner in which the spirocyclic isodicyclopentadienes **14** and **15**[18] react with various iron carbonyl reagents. The question at issue is to what degree and in which direction will π-facial stereoselectivity be demonstrated. We have earlier pointed out the reversal in shielding experienced by the carbon atoms of the spiro ring as detected by ^{13}C NMR (see formulas).[12a] In addition, **14** reacts with a variety of dienophiles from below-plane as does the parent hydrocarbon.[12b] In contrast, spirocyclopentane **15** enters into [4 + 2] cycloaddition totally by top-face bonding.[12b] While we have rationalized this stereochemical crossover in terms of the widely differing σ/π interactions operating within **14** and **15** (as supported by PE studies), Houk has offered an alternative steric interpretation.[19]



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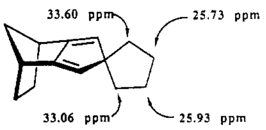

15

The Spirocyclopentane Case Study

When **15** was stirred with $Fe_2(CO)_9$ in tetrahydrofuran or acetonitrile solution at room temperature for 2 days, no complexation was seen to occur as judged by periodic in-

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Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for 16

	x	*y*	*z*	*U*
Fe	4670.9 (5)	1412.7 (4)	2461.3 (4)	45.8 (2)^a
O(1)	5552 (4)	−1189 (3)	2448 (4)	132 (2)^a
O(2)	6942 (4)	3214 (4)	4632 (3)	109 (2)^a
O(3)	6978 (4)	3170 (4)	409 (3)	105 (2)^a
C(1)	5145 (4)	−212 (4)	2465 (4)	75 (2)^a
C(2)	6066 (4)	2494 (4)	3776 (4)	67 (2)^a
C(3)	6080 (4)	2461 (4)	1201 (4)	67 (2)^a
C(4)	3994 (5)	4533 (4)	2318 (5)	79 (2)^a
C(5)	2958 (5)	3603 (4)	3465 (5)	71 (2)^a
C(6)	1182 (5)	3515 (5)	3042 (6)	90 (2)^a
C(7)	1175 (6)	3424 (5)	1511 (5)	86 (2)^a
C(8)	2917 (4)	3466 (4)	1187 (4)	68 (2)^a
C(9)	2811 (4)	2024 (3)	3090 (3)	50 (1)^a
C(10)	2802 (4)	1955 (3)	1685 (3)	49 (1)^a
C(11)	2399 (4)	429 (3)	1300 (3)	47 (1)^a
C(12)	1419 (3)	−579 (3)	2433 (3)	45 (1)^a
C(13)	2424 (4)	544 (3)	3554 (3)	48 (1)^a
C(14)	−475 (4)	−895 (4)	2392 (4)	62 (1)^a
C(15)	−1323 (5)	−2269 (5)	3177 (6)	77 (2)^a
C(15′)	−1369 (22)	−2340 (20)	1965 (17)	55 (5)
C(16)	−424 (5)	−3251 (4)	2782 (6)	101 (2)^a
C(17)	1352 (4)	−2193 (3)	2510 (4)	57 (1)^a

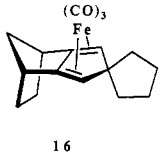
^{a} Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table III. Bond Lengths (Å) for 16

Fe–C(1)	1.785 (4)	C(7)–C(8)	1.543 (7)
Fe–C(2)	1.776 (3)	C(8)–C(10)	1.516 (5)
Fe–C(3)	1.782 (3)	C(9)–C(10)	1.406 (4)
Fe–C(9)	2.050 (4)	C(9)–C(13)	1.415 (4)
Fe–C(10)	2.056 (4)	C(10)–C(11)	1.414 (4)
Fe–C(11)	2.123 (3)	C(11)–C(12)	1.528 (4)
Fe–C(13)	2.113 (3)	C(12)–C(13)	1.532 (4)
O(1)–C(1)	1.140 (6)	C(12)–C(14)	1.550 (5)
O(2)–C(2)	1.149 (5)	C(12)–C(17)	1.541 (5)
O(3)–C(3)	1.140 (5)	C(14)–Cn(15)	1.469 (6)
C(4)–C(5)	1.526 (6)	C(14)–C(15′)	1.344 (17)
C(4)–C(8)	1.534 (5)	C(15)–C(16)	1.515 (8)
C(5)–C(6)	1.567 (7)	C(15′)–C(16)	1.653 (22)
C(5)–C(9)	1.520 (5)	C(16)–C(17)	1.490 (5)
C(6)–C(7)	1.534 (8)		

frared analysis. Recourse instead to refluxing hexane or benzene resulted in the formation of **16**, although in low yield (~10%). As detailed in the Experimental Section, the addition of a small amount of tetrahydrofuran to the hexane (< 1:10) provided for the isolation of **16** as the only observable complex in 50% yield. The infrared spectrum of **16** in hexane solution exhibits carbonyl stretching frequencies at 2020 and 1950 cm^{-1}. Chemical ionization mass spectrometric analysis clearly showed the (M$^+$ + 1) ion at *m/z* 327 in addition to peaks at *m/z* 299, 271, and 243 corresponding to the successive loss of three CO ligands. The ^{1}H and ^{13}C NMR spectra show the molecule to possess C_s symmetry. Furthermore, the deshielded nature of the apical methano carbon (50.8 ppm) relative to the carbons of the ethano bridge (27.7 ppm) implicates coordination of the metal atom to the proximal exo surface.[16,17]

The dark yellow crystals of **16** proved amenable to X-ray analysis (Tables I–IV, Figure 1). It was confirmed not only that complexation had indeed transpired above-plane but also that the metal–ring carbon distances are asymmetric as is customary for isodicyclopentadiene structures. While the unsubstituted trigonal carbons are positioned 1.776–1.785 Å from the iron center, the remaining two that form the fusion point to the norbornyl subunit are more distant at 2.050–2.056 Å.



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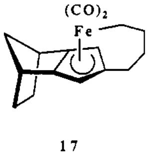

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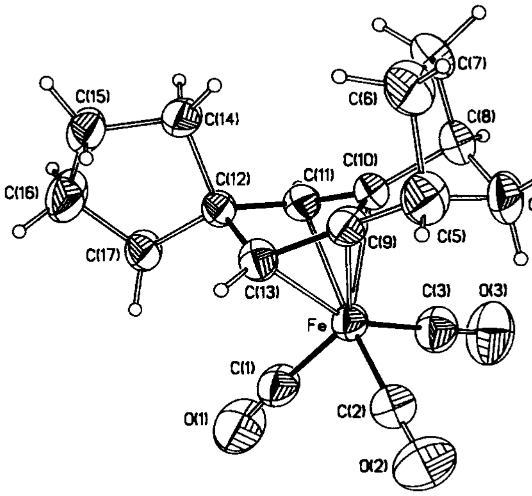

Figure 1. Molecular structure and labeling scheme for **16** drawn with 50% thermal ellipsoids. Disorder occurs at C(15); the majority location is depicted.

Table IV. Bond Angles (deg) for 16

C(1)–Fe–C(2)	99.0 (2)	C(7)–C(8)–C(10)	103.3 (3)
C(1)–Fe–C(3)	98.7 (2)	Fe–C(9)–C(5)	128.2 (2)
C(2)–Fe–C(3)	92.9 (2)	Fe–C(9)–C(10)	70.2 (2)
C(1)–Fe–C(9)	138.9 (2)	C(5)–C(9)–C(10)	106.0 (3)
C(2)–Fe–C(9)	91.9 (2)	Fe–C(9)–C(13)	72.5 (2)
C(3)–Fe–C(9)	120.4 (2)	C(5)–C(9)–C(13)	145.2 (3)
C(1)–Fe–C(10)	136.9 (1)	C(10)–C(9)–C(13)	107.7 (3)
C(2)–Fe–C(10)	122.5 (2)	Fe–C(10)–C(8)	129.3 (2)
C(3)–Fe–C(10)	91.0 (2)	Fe–C(10)–C(9)	69.8 (2)
C(9)–Fe–C(10)	40.1 (1)	C(8)–C(10)–C(9)	107.5 (3)
C(1)–Fe–C(11)	97.4 (1)	Fe–C(10)–C(11)	72.8 (2)
C(2)–Fe–C(11)	157.8 (2)	C(8)–C(10)–C(11)	143.8 (3)
C(3)–Fe–C(11)	99.5 (1)	C(9)–C(10)–C(11)	107.3 (3)
C(9)–Fe–C(11)	65.9 (1)	Fe–C(11)–C(10)	67.7 (2)
C(10)–Fe–C(11)	39.5 (1)	Fe–C(11)–C(12)	93.1 (2)
C(1)–Fe–C(13)	99.3 (1)	C(10)–C(11)–C(12)	107.6 (3)
C(2)–Fe–C(13)	98.0 (1)	C(11)–C(12)–C(13)	95.1 (2)
C(3)–Fe–C(13)	157.2 (2)	C(11)–C(12)–C(14)	112.7 (3)
C(9)–Fe–C(13)	39.7 (1)	C(13)–C(12)–C(14)	113.0 (3)
C(10)–Fe–C(13)	66.3 (1)	C(11)–C(12)–C(17)	118.0 (3)
C(11)–Fe–C(13)	64.4 (1)	C(13)–C(12)–C(17)	116.1 (3)
Fe–C(1)–O(1)	175.6 (3)	C(14)–C(12)–C(17)	102.4 (2)
Fe–C(2)–O(2)	178.1 (4)	Fe–C(13)–C(9)	67.8 (2)
Fe–C(3)–O(3)	178.0 (4)	Fe–C(13)–C(12)	93.3 (2)
C(5)–C(4)–C(8)	96.4 (3)	C(9)–C(13)–C(12)	107.1 (3)
C(4)–C(5)–C(6)	99.5 (4)	C(12)–C(14)–C(15)	105.4 (3)
C(4)–C(5)–C(9)	101.2 (3)	C(12)–C(14)–C(15′)	108.3 (10)
C(6)–C(5)–C(9)	102.7 (3)	C(14)–C(15)–C(16)	103.1 (4)
C(5)–C(6)–C(7)	103.7 (4)	C(15)–C(16)–C(17)	106.6 (3)
C(6)–C(7)–C(8)	104.1 (4)	C(15′)–C(16)–C(17)	97.6 (6)
C(4)–C(8)–C(7)	100.1 (3)	C(12)–C(17)–C(16)	107.3 (3)
C(4)–C(8)–C(10)	100.1 (3)	C(14)–C(15′)–C(16)	102.0 (11)

In a companion study, irradiation of **15** in the presence of Fe(CO)$_5$ was noted to give rise to **16** as well, although the yield was now substantially inferior. Since these conditions appeared to be destructive of the diene, recourse was next made to (benzylideneacetone)iron tricarbonyl, (BDA)Fe(CO)$_3$,[20] in view of the established capacity of this ligand transfer reagent for remarkably high selectivity.[21] The results of heating **15** with excess (BDA)Fe(CO)$_3$ in benzene for 20 h was formation of the ring-opened σ-alkyl

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(20) Howell, J. A. S.; Johnson, B. F. G.; Josty, P. L.; Lewis, J. *J. Organomet. Chem.* **1972**, *39*, 329.

(21) Graham, C. R.; Scholes, G.; Brookhart, M. *J. Am. Chem. Soc.* **1977**, *99*, 1180 and later papers from this research group.

complex **17** in 89% yield. The analogous reaction in refluxing hexane furnished a 1:2 mixture of **16** and **17**.

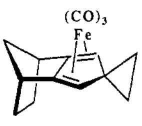
The infrared carbonyl stretching vibrations for **17** are seen at 1990 and 1930 cm^{-1}. The inherent symmetry of this complex is immediately apparent upon inspection of its ^{1}H and ^{13}C NMR spectra. The exo stereochemical assignment follows on similar grounds. In particular, the chemical shift of the apical methano carbon (49.7 ppm) is again notably deshielded relative to those of the ethano bridge (28.1 ppm).

Experiments designed to transform **16** to **17**, thereby providing for independent confirmation of the three-dimensional structural features of the latter, were successful to only a limited degree. Heating of **16** alone in benzene solution or its irradiation in various solvents invariably brought on gradual decomposition. A comparable end result was noted when **16** was heated with trimethylamine *N*-oxide in refluxing benzene.[22] Under similar conditions, but with tetrahydrofuran as solvent, a 20% conversion to **17** was achieved (^{1}H NMR analysis). This low-level reactivity for **16** fits well with the anticipated thermodynamic stability of its spirocyclic five-membered ring.

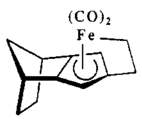
Efforts to effect carbonyl insertion into the Fe–C bond in **17** were to no avail. Stirring **17** with triphenylphosphine in nitromethane (room temperature, 14 days) or in acetonitrile (reflux, 2 days) gave no spectroscopic evidence for reaction, even when a Ce(IV) salt was present as a catalyst.[23] Admixture of **17** with AlCl$_3$ or AlBr$_3$[24,25] provided for significant degradation of the complex.

Ring Cleavage in the Spirocyclopropane Example

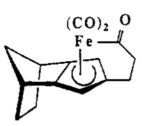
When exposed to similar reaction conditions, the more highly strained spirocyclopropane **14** gave rise to a different spectrum of results, although with identical stereochemical consequences. For example, **18** was never observed in any of the many reactions examined. Under the mildest conditions used, stirring **14** with BDAFe(CO)$_3$ in refluxing dichloromethane solution led directly to **19** in low yield. Once again, it was readily seen that ring cleavage had occurred by virtue of the location of the carbonyl absorptions (1985, 1923 cm^{-1}) and the presence of five (rather than four) trigonal cyclopentadienide carbon atoms (see Experimental Section). The effect of exo coordination was similarly reflected in the appreciable downfield shift of the methano bridge carbon (49.8 ppm).



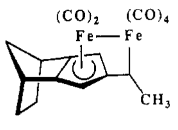
18



19



20



21

On heating **14** with excess (BDA)Fe(CO)$_3$ in benzene, two chromatographically separable products were isolated in yields of 50% and 12%. The major complex has been identified as **20** and the minor as **21**. The latter diiron species was formed uniquely when **14** was refluxed with Fe$_2$(CO)$_9$ in hexane. The infrared spectrum of **20** has strong bands at 2005, 1955, and 1640 cm^{-1}, the latter being characteristic of σ-iron acyl linkage.[10] The ^{1}H NMR spectrum (in C$_6$D$_6$) is in accord with the indicated insertion of a carbonyl group into the bracketing loop. For this system, the apical methano carbon was again strongly deshielded (50.2 ppm) relative to the carbons of the ethano bridge (27.0 ppm).

Table V. Bond Distances (Å) and Angles (deg) for 20

Bond Distances			
Fe–C(1)	2.129 (8)	Fe–C(2)	2.094 (8)
Fe–C(3)	2.078 (8)	Fe–C(4)	2.108 (8)
Fe–C(5)	2.143 (8)	Fe–C(13)	1.956 (8)
Fe–C(14)	1.74 (1)	Fe–C(15)	1.763 (9)
O(1)–C(13)	1.207 (9)	O(2)–C(15)	1.135 (9)
O(3)–C(14)	1.13 (1)	C(1)–C(2)	1.42 (1)
C(1)–C(5)	1.40 (1)	C(1)–C(9)	1.50 (1)
C(2)–C(3)	1.42 (1)	C(3)–C(4)	1.43 (1)
C(3)–C(11)	1.48 (1)	C(4)–C(5)	1.43 (1)
C(5)–C(6)	1.49 (1)	C(6)–C(7)	1.56 (1)
C(6)–C(10)	1.54 (1)	C(7)–C(8)	1.55 (1)
C(8)–C(9)	1.55 (1)	C(9)–C(10)	1.53 (1)
C(11)–C(12)	1.52 (1)	C(12)–C(13)	1.53 (1)
Bond Angles			
C(13)–Fe–C(14)	89.8 (4)	C(13)–Fe–C(15)	88.3 (4)
C(14)–Fe–C(15)	94.8 (4)	C(2)–C(1)–C(5)	109.4 (7)
C(2)–C(1)–C(9)	144.1 (8)	C(5)–C(1)–C(9)	105.9 (7)
C(1)–C(2)–C(3)	107.8 (6)	C(2)–C(3)–C(4)	107.2 (7)
C(2)–C(3)–C(11)	126.2 (7)	C(4)–C(3)–C(11)	125.5 (7)
C(3)–C(4)–C(5)	108.5 (7)	C(1)–C(5)–C(4)	107.2 (7)
C(1)–C(5)–C(6)	107.7 (7)	C(4)–C(5)–C(6)	144.3 (8)
C(5)–C(6)–C(7)	104.5 (7)	C(5)–C(6)–C(10)	100.9 (6)
C(7)–C(6)–C(10)	98.8 (7)	C(6)–C(7)–C(8)	103.7 (7)
C(7)–C(8)–C(9)	102.9 (7)	C(1)–C(9)–C(8)	104.3 (7)
C(1)–C(9)–C(10)	101.8 (7)	C(8)–C(9)–C(10)	100.1 (7)
C(6)–C(10)–C(9)	95.4 (7)	C(3)–C(11)–C(12)	107.8 (7)
C(11)–C(12)–C(13)	110.8 (7)	Fe–C(13)–O(1)	128.8 (8)
Fe–C(13)–C(12)	113.7 (7)	O(1)–C(13)–C(12)	117.4 (7)
Fe–C(14)–O(3)	179 (1)	Fe–C(15)–O(2)	178.2 (9)
C(13)–Fe–Cent	118.2[a]	C(14)–Fe–Cent	126.3
C(15)–Fe–Cent	128.1		

[a] Cent is the centroid of the cyclopentadienyl ring atoms C(1)–C(5).

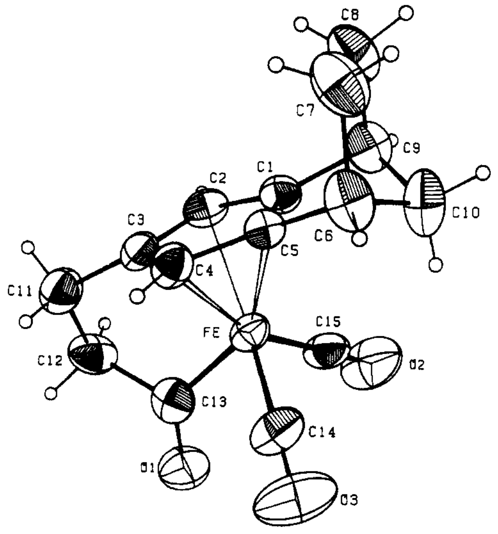


Figure 2. Molecular structure and labeling scheme for **20**.

Ultimate confirmation of the three-dimensional structure of **20** was realized by X-ray crystallography (Tables I, V, and VI, Figure 2) of the yellow solid. Apart from the important stereochemical definition provided by this

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Table VI. Final Fractional Coordinates for 20

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(eq)[a]
Fe	0.17018 (8)	0.27759 (9)	0.06853 (7)	2.10
O(1)	0.2827 (5)	0.1946 (5)	−0.0711 (4)	3.89
O(2)	0.3531 (5)	0.1775 (5)	0.1422 (5)	5.42
O(3)	0.0597 (6)	0.0920 (6)	0.0316 (5)	6.03
C(1)	0.1474 (6)	0.3867 (6)	0.1644 (5)	2.18
C(2)	0.2005 (6)	0.4304 (6)	0.0954 (5)	2.26
C(3)	0.1317 (6)	0.4216 (6)	0.0253 (5)	2.18
C(4)	0.0363 (6)	0.3727 (6)	0.0529 (5)	2.37
C(5)	0.0472 (6)	0.3504 (6)	0.1393 (5)	2.22
C(6)	−0.0115 (6)	0.3175 (7)	0.2153 (5)	3.04
C(7)	−0.0377 (7)	0.4183 (8)	0.2620 (5)	3.79
C(8)	0.0736 (7)	0.4578 (7)	0.2899 (5)	3.72
C(9)	0.1507 (7)	0.3748 (7)	0.2572 (5)	2.98
C(10)	0.0816 (6)	0.2805 (8)	0.2699 (5)	3.63
C(11)	0.1615 (7)	0.4396 (6)	−0.0623 (5)	3.10
C(12)	0.2549 (7)	0.3700 (7)	−0.0830 (5)	3.09
C(13)	0.2438 (6)	0.2682 (8)	−0.0382 (5)	2.77
C(14)	0.1027 (7)	0.1654 (7)	0.0466 (6)	3.39
C(15)	0.2809 (7)	0.2172 (7)	0.1146 (5)	2.90

[a] $B(\mathrm{eq}) = {}^4/_3[a^2b(11) + b^2b(22) + c^2b(33) + ab(\cos\gamma)b(12) + ac(\cos\beta)b(13) + bc(\cos\alpha)b(23)]$.

analysis, it can be seen that the Fe atom in **20** resides at a greater distance from the Cp ring than in **16**. The distances to the unsubstituted trigonal carbons are uniformly greater than 2 Å (viz., 2.078–2.108 Å) and those that have norbornyl character are still more distant (2.129–2.143 Å). This is not surprising since the iron atom is now formally part of a heterocyclic ring.

The fulvene complex **21** is somewhat less stable in solution than **20**, and it has not proven possible to grow crystals of this compound suitable for X-ray investigation. Nevertheless, its IR, mass, and NMR spectra are fully in accord with its suggested structure. Particularly diagnostic are its carbonyl absorptions at 2065, 1985, and 1925 cm^{-1} that compare favorably to those of **7** and its four most downfield ^{1}H signals (in C_6D_6) at δ 3.52 (s), 3.23 (s), 2.44 (d), and 2.03 (q). As in all of the previous examples, the stereochemistry of **21** rests plausibly on the chemical shifts of the methano and ethano bridge carbon atoms. These appear at 49.6 and 27.1 ppm, respectively.

Discussion

An overwhelming preference has been shown for above-plane coordination to **14** and **15** by iron carbonyl reagents. Not observed is the crossover in facial selectivity that characterizes the cycloaddition reactions of these dienes with reactive dienophiles. We conclude that the steric bulk of reagents such as $Fe_2(CO)_9$ and (BDA)$Fe(CO)_3$ is sufficiently demanding that approach from the more congested endo surface does not operate. Also, it is entirely possible that many of these reactions proceed by a mechanism involving initial metal coordination to only one of the two available double bonds, in which case exo stereochemistry would be strongly preferred. An exception could surface in the case of $Fe_2(CO)_9$ because of the metal–metal bonded nature of this reagent. The end result of all these contributions is a stereochemically uniform response by **14** and **15** to coordination by Fe(0) from their exo surface.

When the spiro ring is five-membered as in **15**, η-complexation leading to **11** can be observed because the metal insertion process in this case is insufficiently rapid. Our findings suggest that the existence of **18** is more fleeting. The presence of the strained spirocyclopropane ring so accelerates conversion to the (σ-alkyl)iron complex **19** that **18** could not be detected.

The length of the methylene bridges in **17** and **19** impact as well on the reactivity of the iron-containing loops. We see, for example, that while **17** is kinetically reluctant to undergo carbonyl insertion across the Fe–C σ-bond, **19** is readily transformed into **20**. This is not coincidental. The detailed geometry of **20** as determined crystallographically (Figure 2) provides clear indication that the cyclic array of atoms in the ring containing the acyliron dicarbonyl residue is relatively unstrained. By inference, the bond angles in precursor **19** must be other than optimal. Also, incorporation of an additional carbon atom into the methylene chain of **17** is intuitively expected to enhance global strain because of the increase in loop size and the relative inflexibility associated with the bond lengths from iron to the isodicyclopentadienyl ligand. The restrictions reflected in this sector of the molecule should operate so as to curtail further expansion of the bracket and apparently do so rather effectively.

The comparable mode of iron carbonyl bonding to **14** and **15** has encouraged us to undertake an examination of the compressibility limits of this reaction channel. Presently under investigation is the possibility that placement of suitable syn substituents on the carbon atom of the methano bridge may alter the stereochemical outcome observed here. Whatever the ultimate result, a more in-depth appreciation of steric demands during these reactions will be realized.

Experimental Section

Reaction of 15 with Diiron Enneacarbonyl. To a solution of $Fe_2(CO)_9$ (73 mg, 0.20 mmol) in 10 mL of hexane–tetrahydrofuran (10:1) was added 37 mg (0.20 mmol) of **15**, and the mixture was refluxed under nitrogen for 24 h. The solvent was evaporated, and the residue was chromatographed on activity I alumina (elution with deoxygenated petroleum ether). The yellow band was collected and evacuated to 0.1 Torr to remove $Fe(CO)_5$ and unreacted **15**. There remained 33 mg (50%) of **16**, recrystallization of which from hexanes afforded yellow crystals: mp 87–88 °C; IR (hexane, cm^{-1}) 2020, 1950; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.07 (t, J = 1.7 Hz, 2 H), 2.83 (s, 2 H), 2.16 (dt, J = 3.1, 1.5 Hz, 2 H), 1.90 (t, J = 7.4 Hz, 3 H), 1.63 (dd, J = 7.8, 2.5 Hz, 2 H), 1.55–1.30 (m, 5 H), 0.86 (t, J = 6.8 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) 213.10, 112.14, 75.10, 57.22, 50.84, 46.38, 38.13, 36.33, 27.70, 25.50, 25.25; MS m/z ($M^+ - CO$) calcd 298.0648, obsd 298.0652.

X-ray Crystallographic Analysis of 16. The parameters used during the collection and refinement of diffraction data for **16** are given in Table I. A crystal of **16** was attached to a fine glass fiber with epoxy cement and was found to crystallize in the triclinic crystal system. The centrosymmetric alternative, $P\bar{1}$, was initially assumed and later confirmed by the chemically reasonable and computationally stable results of refinement. An absorption correction was not needed on the basis of a low absorption coefficient, regular crystal shape, and a variation in Ψ-scan intensities of ≤10%.

The location of the Fe atom was obtained by heavy-atom methods. All remaining atoms were found from subsequent difference Fourier syntheses. Non-hydrogen atoms [except C(15′)] were refined anisotropically. C(15) and C(15′) are alternate positions of the same atom (at 81.2% and 18.8% occupancy, respectively). The final difference Fourier synthesis showed only a diffuse background (maximum, 0.35 e/Å^3 near Fe). An inspection of F_o vs F_c values and trends based on sin θ, Miller index, or parity group did not show any systematic errors in the data. All computer programs used in the data collection and refinement are contained in the Nicolet program packages P3 and SHELXTL (version 5.1) (Nicolet XRD, Madison, WI).

Atomic coordinates are provided in Table II and bond lengths and angles in Tables III and IV, respectively.

Conversion of 15 to 17. (Benzylideneacetone)iron tricarbonyl (86 mg, 0.30 mmol) was dissolved in benzene (10 mL) and diene **15** (56 mg, 0.30 mmol) was introduced. After being heated at the reflux temperature under nitrogen for 20 h, the cooled reaction mixture was evaporated and the resulting brown gum was extracted with dichloromethane. Following solvent removal, the residue was purified by chromatography on activity I alumina (elution with pentane). There was isolated 60 mg (89%) of **17** as a yellow oil: IR (benzene, cm^{-1}) 1990, 1930; ^{1}H NMR (300 MHz, C_6D_6) δ 3.68 (s, 2 H), 2.53 (m, 2 H), 1.8–1.7 (m, 3 H), 1.7–1.65 (m, 2 H), 1.65–1.50 (m, 2 H), 1.5–1.3 (m, 4 H), 1.05–0.8 (m, 3 H); ^{13}C NMR (75 MHz, C_6D_6, ppm) 219.39, 112.04, 102.74, 74.25, 49.71, 37.58, 28.78, 28.40, 28.07, 24.54, 5.00; MS *m/z* (M$^+$) calcd 298.0770, obsd 298.0713.

Interconversion of 16 with 17. Trimethylamine *N*-oxide (23 mg, 0.30 mmol) was added to a solution of **16** (100 mg, 0.31 mmol) in tetrahydrofuran (5 mL). The reaction mixture was heated to reflux for 8 h, at which point infrared analysis showed that 10–20% conversion to **17** had materialized. The solvent was evaporated, the residue was filtered through activity I alumina (elution with hexane), and final purification was achieved by chromatography on silica gel (hexane elution). There was isolated 5 mg (7%) of **17** as a yellow oil having spectral properties identical with those described above.

Heating of 14 with (BDA)Fe(CO)$_3$ in Dichloromethane. A solution of **14** (30 mg, 0.19 mmol) in dichloromethane (5 mL) was treated with (benzylideneacetone)iron tricarbonyl (80 mg, 0.30 mmol) and heated at reflux under nitrogen for 2 days. The solvent was evaporated, and the residue was submitted to chromatography on activity I alumina. Elution with hexane resulted in the isolation of **19** as a quite unstable yellow oil (15 mg, 30%): IR (CH_2Cl_2, cm^{-1}) 1985, 1923; ^{1}H NMR (300 MHz, C_6D_6) δ 3.84 (s, 2 H), 2.47 (s, 2 H), 2.23 (t, *J* = 8.2 Hz, 2 H), 1.34 (d, *J* = 8.2 Hz, 2 H), 1.05 (d, *J* = 8.8 Hz, 1 H), 0.8–0.7 (m, 2 H), 0.39 (s, 1 H), –0.35 (t, *J* = 8.3 Hz, 2 H); ^{13}C NMR (75 MHz, C_6D_6 ppm) 120.46, 70.95, 49.75, 37.74, 26.98, 22.47 (carbonyl and quaternary carbons not observed); MS *m/z* (M$^+$) calcd 270.0289, obsd 270.0316.

Heating 14 with (BDA)Fe(CO)$_3$ in Benzene. A solution of (BDA)Fe(CO)$_3$ (0.80 g, mmol) and diene **14** (300 mg, 1.9 mmol) in 50 mL of benzene was heated under nitrogen for 10 h, at which point an additional 500 mg of (BDA)Fe(CO)$_3$ was introduced. Following an additional 10 h of heating, the reaction mixture was cooled and evaporated. The residue was chromatographed on activity I alumina, eluting first with hexane and then ether. There was isolated 280 mg (50%) of **20** and 100 mg (12%) of **21**.

For **20**: sublimed at 60 °C and 1 Torr; yellow crystals; IR (CH_2Cl_2, cm^{-1}) 2005, 1955, 1640; ^{1}H NMR (300 MHz, C_6D_6) δ 4.13 (s, 2 H), 3.19 (t, *J* = 7.7 Hz, 2 H), 2.33 (m, 2 H), 1.5–1.2 (m, 4 H), 1.1–0.7 (m, 4 H); ^{13}C NMR (75 MHz, C_6D_6, ppm) 215.14, 128.54, 112.84, 79.28, 73.24, 50.21, 37.03, 27.01, 20.72; MS *m/z* (M$^+$) calcd 298.0310, obsd 298.0304.

Anal. Calcd for $C_{15}H_{14}FeO_3$: C, 60.43; H, 4.73. Found: C, 60.42; H, 4.75.

For **21**: sublimed at 65 °C and 1 Torr; red crystals; mp 82–84 °C; IR (CH_2Cl_2, cm^{-1}) 2065, 1985, 1925; ^{1}H NMR (300 MHz, C_6D_6) δ 3.52 (s, 1 H), 3.23 (s, 1 H), 2.47 (s, 1 H), 2.42 (s, 1 H), 2.03 (dd, *J* = 13.8, 7.05 Hz, 1 H), 1.5–1.3 (m, 6 H), 1.3–0.8 (m, 3 H); ^{13}C NMR (75 MHz, C_6D_6, ppm) 214.38, 114.69, 113.32, 101.12, 66.45, 65.47, 49.60, 37.33, 37.24, 27.08, 23.58, 13.79; MS *m/z* (M$^+$) calcd 437.9488, obsd 437.9466.

Anal. Calcd for $C_{18}H_{14}Fe_2O_6$: C, 49.36; H, 3.22. Found: C, 49.81; H, 3.43.

X-ray Crystallographic Analysis of 20. A yellow single crystal fragment of **20** was mounted on a pin and transferred to the goniometer. The space group was determined to be the centric Pbca from the systematic absences. A summary of data collection parameters is given in Table I.[26,27] Least-squares refinement with isotropic thermal parameters led to *R* = 0.084. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with *B* fixed at 5.5 Å^2. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of *R* = 0.048 and R_w = 0.048. Bond distances and angles are compiled in Table V. The final values of the positional parameters are given in Table VI.

Reaction of 14 with Diiron Enneacarbonyl. A mixture of $Fe_2(CO)_9$ (1.0 g, excess and **14** (300 mg, 1.9 mmol) in hexane (50 mL) was heated at reflux under nitrogen for 6 h. Additional $Fe_2(CO)_9$ (500 mg) was introduced, and heating was continued for 10 h. The cooled reaction mixture was evaporated, the residue was chromatographed on activity I alumina, and the purified product was sublimed at 95 °C and 1 Torr to give 210 mg (26%) of **21**.

Acknowledgment. We thank the National Institutes of Health for support of this research program through Grant CA-12115. G.A.O. is the recipient of a Department of Education-sponsored National Need Fellowship.

Registry No. **14**, 81897-89-4; **15**, 81897-93-0; **16**, 121962-53-6; **17**, 121935-63-5; **19**, 121935-64-6; **20**, 121935-65-7; **21**, 121935-66-8; $Fe_2(CO)_9$, 15321-51-4; (BDA)Fe(CO)$_3$, 38333-35-6; trimethylamine *N*-oxide, 1184-78-7.

Supplementary Material Available: Tables of hydrogen atom coordinates and anisotropic thermal parameters for **16** and **20** and a table of least-squares planes for **20** (6 pages); listings of observed and calculated structure factors for **16** and **20** (15 pages). Ordering information is given on any current masthead page.

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[27] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72, 99, 149.