and poured over 100 g of crushed ice. The mixture was extracted with 3 × 100 mL of ether. The combined ethereal extract was washed with $H_2O$ (50 mL), 10% aqueous $NaHCO_3$ solution (2 × 50 mL), water (50 mL), and aqueous $Na_2S_2O_3$ solution (50 mL). The ethereal solution was dried ($MgSO_4$), filtered, and stripped of solvent to afford a crude solid. Recrystallization from benzene/hexane afforded 34.5 g of ethyl ester **2b** (118 mmol, 78% yield): mp, 81–82 °C; NMR $\delta_{CDCl_3}$ 7.80 (d, $J = 8$ Hz, 1 H, aryl), 7.33 (d, $J = 3$ Hz, 1 H, aryl), 6.73 (dd, $J = 3, 8$ Hz, 1 H, aryl), 4.40 (q, $J = 7$ Hz, 2 H, O$CH_2$), 1.37 (t, $J = 7$ Hz, 3 H, $CH_3$).

To a solution of sodium ethoxide, prepared by dissolving 1.73 g (75.2 mmol) of sodium in 100 mL of ethanol, was slowly added 20.0 g (68.5 mmol) of ethyl ester **2b**. This solution was added over 4 h to a stirred, refluxing solution containing 38.6 g (205 mmol) of 1,2-dibromoethane in 100 mL of ethanol. Stirring and refluxing were continued for an additional 4 h. The reaction mixture was cooled and filtered (to remove NaBr) and then stripped of ethanol and excess dibromoethane. The crude product (**2c**) was taken up in 250 mL of benzene, washed with cold 10% aqueous NaOH solution (2 × 50 mL), and dried over $MgSO_4$. Solvent was stripped, and the residue was chromatographed ($SiO_2$, 1:5 EtOAc/hexane) to afford 14.8 g (37.1 mmol, 54%) of pure bromoethyl ether **2c**: NMR $\delta_{CDCl_3}$, 7.90 (d, $J = 8$ Hz, 1 H, aryl), 7.40 (d, $J = 3$ Hz, 1 H, aryl), 6.80 (dd, $J = 3, 8$ Hz, 1 H, aryl), 4.63–4.23 (q + t, 7 H, $CH_2O + CH_2O$), 3.67 (t, $J = 6$ Hz, 3 H, $CH_2Br$), 1.43 (t, $J = 7$ Hz, $CH_3$).

Anal. Calcd for $C_{11}H_{12}BrIO_3$: C, 33.09; H, 3.03; Br, 20.03. Found: C, 33.08; H, 3.07; Br, 20.12.

Bromo ether **2c**, 12.0 g (30.1 mmol) and 9.4 g (34.9 mmol) of *N*-(*n*-hexadecyl)-*N*,*N*-dimethylamine (Ethyl Corp.) were refluxed in 150 mL of ethanol for 3 days. Ethanol was removed under reduced pressure, and the residue was stirred in 200 mL of dry ether for 2 h. Filtration (sintered glass) afforded a white solid that was washed with 100 mL of dry ether and recrystallized from EtOAc, yielding 15.2 g (22.7 mmol, 75%) of quaternary salt **2d**: mp 101–102 °C; NMR $\delta_{Me_2SO\text{-}d_6}$ 7.90 (d, $J = 8$ Hz, 1 H, aryl), 7.29 (d, $J = 3$ Hz, 1 H, aryl), 6.93 (dd, $J = 3, 8$ Hz, 1 H aryl), 4.54–4.21 (m + q, 4 H, $CH_2O + CO_2CH_2$), 3.80 (m, 2 H, $N^+CH_2CH_2O$), 3.45–3.20 (m + br s at 3.32, 8 H, $CH_2N^+Me_2$), 1.33 (t, $J = 7$ Hz, 3 H, $CO_2CH_2CH_3$), 1.24 (br s, 28 H $(CH_2)_{14}$), 0.85 ("t", 3 H, term. $CH_3$).

Anal. Calcd for $C_{29}H_{51}BrINO_3$: C, 52.10; H, 7.69; I, 18.98. Found: C, 52.13; H, 7.75; I, 19.12.

Quaternary salt–ethyl ester **2d** was saponified by refluxing 10.0 g (15.0 mmol) in 60 mL of methanol and 10 mL of 2 N aqueous NaOH. The reaction mixture was cooled and acidified with dilute HCl. Ethanol and water were removed under reduced pressure, the residue was taken up in 50 mL of dry ethanol, and NaCl was removed by filtration. Ethanol was stripped to give a sticky yellow solid, which was recrystallized from EtOH/EtOAc, affording 9.1 g (14.2 mmol, 95%) of white quaternary salt/iodo acid **2e** as the bromide salt, mp 103–105 °C. The NMR spectrum of **2e** is very similar to that of **2d** (see above), but the former lacks the signals of the ethyl ester group.

Anal. Calcd for $C_{27}H_{47}BrINO_3$: C, 50.63; H, 7.40; I, 19.81. Found: C, 50.57; H, 7.57; I, 19.72.

Oxidation of **2e** to iodosobenzoate surfactant **1c** was carried out in accord with the chlorination/hydrolysis procedure described in ref 12 and 13. In this way, 5.0 (7.8 mmol) of **2e** was oxidized to 3.8 g (6.2 mmol, 79%) of slightly yellow crystalline **1c**, isolated as the *chloride* salt, mp 125–128 °C. This material showed 98 ± 4% of iodosyl activity by $KI/Na_2S_2O_3$ iodometric titration.[13]

Anal. Calcd for $C_{27}H_{47}ClINO_4$: C, 52.98; H, 7.74; Cl, 5.79. Found: C, 53.25; H, 7.68; Cl, 5.53.

**Kinetic Studies.** Solutions of **1c**/CTACl were prepared by sonication (Braun Sonic Model 1510 sonicator, small immersion probe, 80 W, 10 min, 50–55 °C) in 0.01 M pH 8.0 Tris buffer, $\mu = 0.01$ (KCl). All kinetic runs employed freshly prepared catalyst solutions.

Slower reactions were followed on a Gilford Model 250 spectrophotometer coupled to a Gilford Model 6051 recorder. Faster reactions were followed on a Durrum Model D-130 stopped-flow spectrophotometer coupled either to a Tektronix Model 5103N/D15 storage oscilloscope or, via a custom-built interface, to a Commodore Model 8032 computer. Constant-temperature circulating baths maintained reaction temperatures at 25 ± 0.1 °C. All buffers were prepared from Steam-Distilled water (distilled, U.S.P., Electrified Water Co., East Orange, NJ). Rate constants were obtained from computer-generated correlations of log $(A_\infty - A_t)$ with time for the appearance of *p*-nitrophenoxide ion at 400 nm. Conditions for all the kinetic runs are described in the Results section. Rate constants are tabulated in Tables I–III of the supplementary material and presented graphically in Figures 1–3. Micellar reactions were followed to >90% completion and showed good first-order kinetics ($r > 0.999$). Reproducibilities of the rate constants were <±3%. Values of $k_\psi^{max}$ appear in Table I. Turnover experiments are summarized in Table II.

**Acknowledgments.** We thank S. Chatterjee for technical assistance. We are grateful to the US Army Research Office and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

**Registry No.** **1c** chloride, 99665-69-7; **2a**, 57772-57-3; **2b**, 99665-70-0; **2c**, 99665-71-1; **2d**, 99665-72-2; **2e**, 99665-73-3; **3**, 10359-36-1; **4**, 311-45-5; **5**, 7364-83-2; 1,2-dibromoethane, 106-93-4; *N*-(*n*-hexadecyl)-*N*,-*N*,-dimethylamine, 112-69-6.

**Supplementary Material Available:** Tables I–III containing (respectively) rate constants for cleavages of PNPDPP, PNPDEP, and PNPIMP by **1c**/CTACl (3 pages). Ordering information is given on any current masthead page.

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# Reactions of Coordinated Molecules. 42. Diels–Alder Reactions Utilizing (Ferra-$\beta$-diketonato)$BF_2$ Complexes Containing Alkenyl Substituents as Activated Dienophiles

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**Abstract:** Three (ferra-$\beta$-diketonato)$BF_2$ complexes having alkenyl substituents attached to the ferra-chelate ring react as activated dienophiles in Diels–Alder cycloaddition reactions. Ten Diels–Alder adducts are prepared and characterized. The dienes used include isoprene, 2,3-dimethyl-1,3-butadiene, *trans*-2-methyl-1,3-pentadiene, and cyclopentadiene. The X-ray structures of one reactant complex having a methacryl substituent and its cycloaddition adducts with isoprene and *trans*-2-methyl-1,3-pentadiene are reported. These Diels–Alder reactions proceed in good to high yield with a regioselectivity consistent with the analogous reactions of methyl methacrylate and crotonic acid. Furthermore, due to the highly asymmetric Fe center within the methacrylate dienophile, diene cycloaddition occurs with unusually high stereoselectivity when diastereomeric adducts are formed.

The preparation and characterization of (ferra-$\beta$-diketonato)boron difluoride complexes,[2,3] **1**, and related compounds[4,5] led to the discovery of an unusual interligand C–C bond formation reaction upon deprotonation of a ferra-chelate ring substituent

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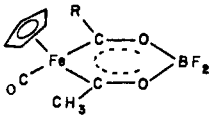
at the α-carbon atom.[6-8] The facility of this deprotonation is presumably related to the stabilization of the formal α-enolate anion **2** by the ferra-β-diketonate ring and the $BF_2$ moiety.[9] By



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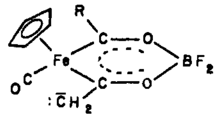

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similar reasoning, if the exomethylene group of **2** were replaced by an alkenyl substituent, then the chelate ring carbonyl functionality and the coordinated $BF_2$ group might activate the alkenyl C–C double bond toward cycloaddition reactions. These organometallic complexes might then exhibit chemical reactivity analogous to that of Lewis acid adducts of acrylic acid esters and related derivatives.

We now report a general study of the Diels–Alder cycloaddition chemistry of methacrylate and crotonate derivatives of (ferra-β-diketonato)$BF_2$ complexes.[10] These compounds act as dienophiles, and their reactions with isoprene, 2,3-dimethyl-1,3-butadiene, *trans*-2-methyl-1,3-pentadiene, and cyclopentadiene are discussed. The structures of the addition products are elucidated by $^1H$ NMR and X-ray crystallography. Kinetic data reveal that a methacrylate (ferra-β-diketonato)$BF_2$ complex adds to 2,3-dimethylbutadiene at a rate approximately 50 times faster than the rate of addition of this diene to methyl methacrylate.

## Experimental Section

All reactions and other manipulations were performed under dry, prepurified nitrogen. Diethyl ether, pentane, hexane, and tetrahydrofuran (THF) were dried over Na/K alloy, with benzophenone having been added to the diethyl ether and THF. Methylene chloride was dried over $P_2O_5$. All solvents were distilled under nitrogen before use.

Infrared (IR) spectra were recorded on a Perkin-Elmer 727 spectrometer as either pentane, hexane, or methylene chloride solutions in 0.10-mm sodium chloride cavity cells with the solvent as a reference and a polystyrene film as a calibration standard. Solid-state IR spectra were recorded on the same instrument by using KBr pellets of the samples. Routine $^1H$ NMR spectra were obtained on either a JEOL MH-100 or a JEOL FX90Q NMR spectrometer as $CDCl_3$ solutions with $Me_4Si$ as an internal reference. $^{13}C$ NMR and high-field $^1H$ NMR spectra were obtained on a Bruker AM-400 NMR spectrometer. Microanalyses were performed by MicAnal Organic Microanalysis, Tucson, AZ.

The compounds ($\eta$-$C_5H_5$)$(OC)_2$Fe{[$H_2C$=C(Me)]C(O)} (**3**) and ($\eta$-$C_5H_5$)$(OC)_2$Fe{[*trans*-(H)(Me)C=C(H)]C(O)} (**4**) were prepared by literature methods.[11]

**Preparation of ($\eta$-$C_5H_5$)(OC)Fe(MeCO){[$H_2C$=C(Me)]CO}$BF_2$ (5).** To a stirred solution of 2.5 g (10.1 mmol) of **3** in 30 mL of diethyl ether at −78 °C was added dropwise 6.9 mL of a 1.5 M solution of methyllithium in ether. The solution was allowed to warm slowly in a dry ice/acetone bath over a period of 3 h. The bath was then removed, and the solution was allowed to warm to room temperature. The solvent was removed at reduced pressure by using a warm water bath. $CH_2Cl_2$ (90 mL) was added to the residue to produce a light brown suspension which was then cooled to 0 °C. Gaseous $BF_3$ was bubbled through the suspension at a moderate rate for 50 s, and the suspension became brown-orange in color. The 0 °C bath was removed; and the solution was allowed to warm to room temperature. Then the solution was pumped to dryness at reduced pressure. The residue was extracted with 200 mL of ether. The extracted solution was filtered and chromatographed through a 13-cm column of Florisil in hexane. A mixture of ether/hexane (30/70) was used to elute a yellow-brown band which was concentrated until it was slightly turbid. Crystallization at −20 °C afforded 1.49 g (55%) of yellow-orange crystals: mp 82–83 °C; IR ($CH_2Cl_2$) $\nu$(CO) 2010 (w), 1975 (s) $cm^{-1}$; IR (hexane) $\nu$(CO) 1975 (vs) $cm^{-1}$; IR (KBr pellet) $\nu$(CO) 2000 (vs) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.94 (s, 3, MeC=C), 2.86 (s, 3, MeCO), 4.76 (s, 5, $C_5H_5$), 5.94 (d, 2, $CH_2$=C, $J$ = 5.6 Hz). Anal. Calcd for $C_{12}H_{13}O_3BF_2Fe$: C, 46.50; H, 4.24. Found: C, 46.45; H, 4.38. The X-ray structure of **5** is reported below.

**Preparation of ($\eta$-$C_5H_5$)(OC)Fe(PhCO){[$H_2C$=C(Me)]CO}$BF_2$ (6).** To a stirred solution of 2.74 g (11.1 mmol) of **3** in 50 mL of diethyl ether at −78 °C was added dropwise 4.7 mL of a 2.4 M solution of phenyllithium in cyclohexane/diethyl ether (70/30). The solution was allowed to warm slowly in a dry ice/acetone bath over a period of 3 h during which time a yellow solid precipitated from the red solution. The bath then was removed, and the solution was allowed to warm to room temperature. The solvent was removed at reduced pressure by using a warm water bath. $CH_2Cl_2$ (90 mL) was added to the residue to produce a light brown suspension which was then cooled to 0 °C. Gaseous $BF_3$ was bubbled through the suspension at a moderate rate for 60 s. The 0 °C bath was removed, and the rust-colored solution obtained was allowed to warm to room temperature. The solution was then pumped to dryness at reduced pressure, and the residue was extracted with 200 mL of diethyl ether. The extracted solution was filtered, concentrated, and chromatographed through a 13-cm column of Florisil in hexane. A mixture of ether/hexane (40/60) was used to elute a reddish-brown band. The solvent was removed at reduced pressure to yield 2.73 g (66%) of a red oil: IR (hexane) $\nu$(CO) 1975 (vs) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.97 (s, 3, *Me*C=$CH_2$), 4.73 (s, 5, $C_5H_5$), 6.15 (d, 2, $CH_2$=C, $J$ = 16.5 Hz), 7.33, 7.39, 7.50, 7.57, 7.99, 8.05 (m, 5, $C_6H_5$). Anal. Calcd for $C_{17}H_{15}O_3BF_2Fe$: C, 54.89; H, 4.07. Found: C, 54.61; H, 4.25.

**Preparation of ($\eta$-$C_5H_5$)(OC)Fe(MeCO){[*trans*-(H)(Me)C=C(H)]CO}$BF_2$ (7).** To a stirred solution of 2.96 g (12.01 mmol) of **4** in 80 mL of diethyl ether at −78 °C was added dropwise 8.01 mL of a 1.5 M solution of methyllithium in ether. The solution was allowed to warm slowly in a dry ice/acetone bath over a period of 3 h. The bath was then removed, and the solution was allowed to warm to room temperature. The solvent was removed at reduced pressure by using a warm water bath. $CH_2Cl_2$ (140 mL) was added to the residue to produce an orange-brown solution which was then cooled to 0 °C. Gaseous $BF_3$ was bubbled through the solution at a moderate rate for 60 s to give an orange-brown suspension. The 0 °C bath was removed, and the solution was allowed to warm to room temperature. Then the solution was pumped to dryness at reduced pressure. The residue was extracted with 200 mL of ether. The extracted solution was filtered and chromatographed through a 13-cm column of Florisil in hexane. Ether was used to elute an orange band which was concentrated until it was slightly turbid. Crystallization at −20 °C afforded 0.68 g (18%) of red-orange crystals: mp 94–96 °C; IR ($CH_2Cl_2$) $\nu$(CO) 1990 (s), 1960 (s) $cm^{-1}$; IR (KBr pellet) $\nu$(CO) 1995 (vs) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.85 (d, 3, C=C(Me), $J$ = 6.0 Hz), 2.86 (s, 3, MeCO), 4.91 (s, 5, $C_5H_5$), 6.73, 6.79, 6.85, 6.99 (m, 2, HC=CH). Anal. Calcd for $C_{12}H_{13}O_3BF_2Fe$: C, 46.50; H, 4.24. Found: C, 46.62; H, 4.38.

**General Preparation of ($\eta$-$C_5H_5$)(OC)Fe(RCO){[$CH_2CH_2$(Me)-C=C(H)$CH_2$(Me)C]CO}$BF_2$ where R is Me or Ph (5a, 6a).** To 0.25–0.35 g of either **5** or **6** was added 5 mL of isoprene. The reaction solution was stirred at room temperature as a closed system for 24 h. The isoprene was then removed at reduced pressure, and the residue was extracted with 2 mL of ether. The product was isolated as either a crystalline solid or an oil by precipitation from an ether/pentane solution at −20 °C following chromatography on a 13-cm Florisil column in hexane using ether/hexane (1:4) for band elution. The characterization data for each complex are provided below.

($\eta$-$C_5H_5$)(OC)Fe(MeCO){[$CH_2CH_2$(Me)C=C(H)$CH_2$(Me)C]CO}-$BF_2$ (**5a**): amber needles (38%, crude yield 82%); mp 60–61 °C; IR (pentane) $\nu$(CO) 1963 (vs) $cm^{-1}$; IR (KBr pellet) $\nu$(CO) 1960 (vs) $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.01 (s, 3, MeCCO), 1.55, 1.66, 1.67, 1.68, 1.69, 1.93, 2.33, 2.39 (m, 6, ring $CH_2$ protons), 1.64 (br s, 3, *Me*C=CH), 2.83 (s, 3, MeCO), 4.71 (s, 5, $C_5H_5$) 5.31 (br s, 1, C*H*=CMe); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.5 (q, *Me*CCO), 23.0 (q, *Me*C=CH), 27.4 (t, $CH_2$), 31.9

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(t, $CH_2$), 35.5 (t, $CH_2$), 49.8 (q, *Me*CO), 59.5 (s, Me*C*CO), 84.9 (d, $C_5H_5$), 118.8 (d, CH), 132.7 (s, CH=*C*$CH_3$), 215.8 (s, CO), 344.0 (s, Me*CO*), 355.7 (s, Me*C*CO). Anal. Calcd for $C_{17}H_{21}O_3BF_2Fe$: C, 54.01; H, 5.61. Found: C, 53.67; H, 5.52.

**($\eta$-$C_5H_5$)(OC)Fe(PhCO){[$CH_2CH_2$(Me)C=C(H)$CH_2$(Me)C]CO}-$BF_2$ (6a)**: red-black oil (84%); IR (pentane) $\nu$(CO) 1963 (vs) cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.06 (s, 3, *Me*CCO), 1.68 (br s, 3, *Me*C=CH), 1.75, 1.78, 1.98, 2.33 (m, 6, ring $CH_2$ protons), 4.78 (s, 5, $C_5H_5$), 5.32 (br s, 1, *CH*=$CCH_3$), 7.33, 7.42, 7.50, 7.59, 8.00, 8.07 (m, 5, $C_6H_5$). Anal. Calcd for $C_{22}H_{23}O_3BF_2Fe$: C, 60.03; H, 5.28. Found: C, 59.53; H, 5.31.

**General Preparation of ($\eta$-$C_5H_5$)(OC)Fe(RCO){[$CH_2CH_2$(Me)-C=C(Me)$CH_2$(Me)C]CO}$BF_2$ where R is Me or Ph (5b, 6b).** To 0.30–0.45 g of either **5** or 6 was added 5 mL of 2,3-dimethyl-1,3-butadiene. The resulting solution was allowed to stir at room temperature for 17 h. The 2,3-dimethyl-1,3-butadiene was removed at reduced pressure, and the residue was chromatographed through a 13-cm Florisil column by using 20–50% ether/80–50% hexane to elute the product. The product crystallized from ether/pentane solution at −20 °C. The characterization data for each complex are provided below.

**($\eta$-$C_5H_5$)(OC)Fe(MeCO){[$CH_2CH_2$(Me)C=C(Me)$CH_2$(Me)C]CO}-$BF_2$ (5b)**: yellow-orange needles (32%, crude curde yield 87%); mp 137 °C; IR (pentane) $\nu$(CO) 1969 (vs) cm$^{-1}$; IR (KBr pellet) $\nu$(CO) 1963 (vs) cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.96 (s, 3, *Me*CCO), 1.55, 1.64, 1.65, 1.67, 1.70, 1.87, 1.92, 2.00, 2.10 (m, 4, ring $CH_2$ protons), 1.58, 1.60 (two singlets, 6, *Me*C=C*Me*), 1.81, 2.26 (two doublets, 2, (MeC*$CH_2$*C(Me), *J* = 20 Hz), 2.84 (s, 3, MeCO), 4.71 (s, 5, $C_5H_5$). Anal. Calcd for $C_{18}H_{23}O_3BF_2Fe$: C, 55.14; H, 5.92. Found: C, 54.82; H, 5.70.

**($\eta$-$C_5H_5$)(OC)Fe(PhCO){[$CH_2CH_2$(Me)C=C(Me)$CH_2$(Me)C]CO}-$BF_2$ (6b)**: brown needles (44%, crude yield 87%); mp 130–132.5 °C; IR (pentane) $\nu$(CO) 1965 (vs) cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.00 (s, 3, MeCCO), 1.26, 1.84, 1.99, 2.26, 2.42, 2.60 (m, 6, ring $CH_2$ protons), 1.64 (br s, 6, *Me*C=C*Me*), 4.77 (s, 5, $C_5H_5$), 7.41, 7.50, 7.92, 8.01 (m, 5, $C_6H_5$). Anal. Calcd for $C_{23}H_{25}O_3BF_2Fe$: C, 60.82; H, 5.56. Found: C, 60.76; H, 5.54.

**Preparation of ($\eta$-$C_5H_5$)(OC)Fe(MeCO){[(Me)(H)C$CH_2$(Me)C=C(Me)$CH_2$C(H)]CO}$BF_2$ (7a).** To 0.34 g (1.1 mmol) of 7 was added 3 mL of benzene and 5 mL of 2,3-dimethyl-1,3-butadiene. The resulting solution was allowed to stir at room temperature for 96 h. The solvent was removed at reduced pressure, and the ether extract of the residue was chromatographed through a 13-cm Florisil column by using an ether/hexane (40/60) solution to elute the product. Precipitation at −20 °C afforded 0.146 g (8%) of pale yellow powder: mp 160 °C dec; IR ($CH_2Cl_2$) $\nu$(CO) 2010 (s) cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 0.80 (d, 3, *Me*CH, *J* = 5.9 Hz), 1.58 (s, 6, *Me*C=C*Me*), 1.93 (br m, 5, ring $CH_2$ protons and C*H*Me), 2.86 (s, 3, MeCO), 3.54, 3.62 (m, 1, CHCO), 4.99 (s, 5, $C_5H_5$). Anal. Calcd for $C_{18}H_{23}O_3BF_2Fe$: C, 55.14; H, 5.92. Found: C, 52.61; H, 5.

**General Preparation of ($\eta$-$C_5H_5$)(OC)Fe(RCO){[$CH_2CH_2$(Me)-C=C(H)CH(Me)C(Me)]CO}$BF_2$ where R is Me or Ph (5c or 6c).** To 0.26–0.29 g of either **5** or **6** was added 3.5 mL of *trans*-2-methyl-1,3-pentadiene. The resulting solution was stirred at room temperature for 24 h. The diene was then removed at reduced pressure. The reaction residue was dissolved in a minimum volume of ether, and this solution was chromatographed on a 13-cm Florisil column in hexane. The product was eluted by using an ether/hexane solution ($^1/_4$). Crystallization of the product from ether/pentane solution at −20 °C gave crystalline material. The characterization data for each complex are provided below.

**($\eta$-$C_5H_5$)(OC)Fe(MeCO){[$CH_2CH_2$(Me)C=CHCH(Me)C(Me)]-CO}$BF_2$ (5c)**: orange crystals (34%, crude yield 75%); mp 116–119 °C; IR (pentane) $\nu$(CO) 1970 (vs) cm$^{-1}$: $^1$H NMR ($CDCl_3$) $\delta$ 0.73 (d, 3, *Me*CH, *J* = 6.2 Hz), 0.86 (s, 3, MeCCO), 1.55, 1.83, 2.00, 2.05, 2.07 (m, 4, ring $CH_2$ protons), 1.64 (br s, 3, *Me*C=CH), 2.50 (m, 1, C*H*Me), 2.85 (s, 3, MeCO), 4.68 (s, 5, $C_5H_5$), 5.25 (m, 1, CH). Anal. Calcd for $C_{18}H_{23}O_3BF_2Fe$: C, 55.14; H, 5.92. Found: C, 55.15; H, 5.94.

**($\eta$-$C_5H_5$)(OC)Fe(PhCO){[$CH_2CH_2$(Me)C=CHCH(Me)C(Me)]CO}-$BF_2$ (6c)**: red-black crystals (26%, crude yield 75%); mp 168–172 °C; IR (pentane) $\nu$(CO) (1967 (vs) cm$^{-1}$; $^1$H NMR 0.71 (d, 3, *Me*CH, *J* = 7.4 Hz), 0.91 (s, 3, MeCCO), 1.64 (br s, 3, MeC=CH), 2.02 (br s, 4 ring $CH_2$ protons), 2.47 (m, 1, C*H*Me), 4.76 (s, 5, $C_5H_5$), 5.20, 5.26 (m, 1, CH), 7.33, 7.40, 7.51, 7.57, 7.95, 8.03 (m. 5. $C_5H_6$). Anal. Calcd for $C_{23}H_{25}O_3BF_2Fe$: C, 60.82; H, 5.56. Found: C, 60.79; H, 5.62.

**General Preparation of ($\eta$-$C_5H_5$)(OC)Fe(RCO)[(5-methyl-5-norborn-2-ene)CO]$BF_2$ where R is Me or Ph (5d or 6d).** Dicyclopentadiene was cracked thermally by a literature method.[12] Approximately 0.36–0.39 g of either **5** or 6 was dissolved in 10 mL of cyclopentadiene, and the reaction solution was stirred for 24 h at room temperature. The solvent was evaporated at reduced pressure, and the residue was extracted into a minimum volume of ether. This solution was chromatographed on a Florisil column in hexane, and the product was eluted with an ether/hexane ($^1/_9$) solution. Pure products was obtained by precipitation from ether/pentane solution at −20 °C. The characterization data for each complex are provided below.

**($\eta$-$C_5H_5$)(OC)Fe(MeCO)[(5-methyl-5-norborn-2-ene)CO]$BF_2$ (5d)**: yellow oil (98%, endo/exo ratio ca. 1:1). The endo isomer can be crystallized eventually at −20 °C as tan crystals (mp 128–133 °C) with the supernatant solution being enriched in the exo isomer (which affords an oil upon concentration at reduced pressure). IR (pentane) $\nu$(CO) 1975 (vs) cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ endo isomer: 0.76 (s, 3, MeCCO), 0.86, 0.95, 1.03, 1.13, 1.27, 1.39, 1.45 (m, 4, 4 ring $CH_2$ protons), 2.85 [br s, 4, MeCO and $CH_a$ (bridgehead)], 3.36 (br s, 1, $CH_d$ (bridgehead)], 4.67 (s, 5, $C_5H_5$), 6.12, 6.27 (m, 2, HC=CH); exo isomer: 0.90–1.35, 1.50, 1.56, 1.81, 1.93, 2.35, 2.47 (m, 4, 4 ring $CH_2$ protons), 1.01 (s, 3, MeCCO), 2.81 [br s, 4, MeCO and $CH_a$ (bridgehead)], 3.11 [br s, 1, $CH_d$ (bridgehead)], 4.54 (s, 5, $C_5H_5$), 6.12 (m, 2, HC=CH). Anal. Calcd for $C_{17}H_{19}O_3BF_2Fe$: C, 54.30; H, 5.10. Found: C, 54.23; H, 5.09.

**($\eta$-$C_5H_5$)(OC)Fe(PhCO){(5-methyl-5-norborn-2-ene)CO}$BF_2$ (6d)**: orange-brown powder consisting of a mixture of both the endo and exo isomers (52%); mp 134–137 °C; IR [pentane/$CH_2Cl_2$ (1/1)] $\nu$(CO) 1967 (vs) cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ endo isomer: 0.75 (s, 3, MeCCO), 0.90–1.56 (m, 4, 4 ring $CH_2$ protons), 2.91 [br s, 1, $CH_a$ (bridgehead)], 3.39 [br s, 1, $CH_d$ (bridgehead)], 4.81 (s, 5, $C_5H_5$), 6.19 6.33 (m, 2, HC=CH), 7.34, 7.44, 7.51, 7.58, 7.97, 8.03 (m, 5, $C_6H_5$); exo isomer: 0.90–1.35, 1.50, 1.56, 1.80, 1.93, 2.44, 2.56 (m, 4, 4 ring $CH_2$ protons), 1.02 (s, 3, MeCCO) , 2.91 [br s, 1, $CH_a$ (bridgehead)], 3.15 [br s, 1, $CH_d$ (bridgehead)], 4.72 (s, 5, $C_5H_5$), 6.19 (m, 2, HC=CH), 7.34, 7.44, 7.51, 7.58, 7.97, 8.03 (m, 5, $C_6H_5$). Anal. Calcd for $C_{22}H_{21}O_3BF_2Fe$: C, 60.31; H, 4.84. Found: C, 59.21; H, 4.96.

**Preparation of *endo*-($\eta$-$C_5H_5$)(OC)Fe(MeCO)[(6-methyl-5-norborn-2-ene)CO]$BF_2$ (7b).** To 15 mL of cyclopentadiene was added 0.40 g (1.3 mmol) of 7. The resulting solution was stirred for 48 h at room temperature. The excess cyclopentadiene was removed at reduced pressure, and the resulting brown oil was extracted with a minimum volume of ether. The extracted solution was chromatographed through a 13-cm column of Florisil in hexane. The product was eluted with ether and was crystallized from a concentrated ether solution at −20 °C to yield 0.24 g (49%) of bright yellow crystals: mp 144–145 °C; IR (pentane) $\nu$(CO) 1995 (w), 1960 (s) cm$^{-1}$; IR ($CH_2Cl_2$) $\nu$(CO) 1985 (s), 1960 (s) cm$^{-1}$; IR (KBr pellet) $\nu$(CO) 2000 (vs) cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.09 (d, 3, *Me*CHCH, *J* = 6.7 Hz), 1.36 (m, 1, $H_{anti}$), 1.60 (m, 1, $H_{syn}$), 1.88, 1.96, 2.02, 2.10 (m, 1, MeC*$H_f$*, *J* = 6.6 Hz), 2.50 [br s, 1, $H_a$ (bridgehead)], 2.83 (s, 3, MeCO), 3.15 [br s, 1, $H_d$ (bridgehead)], 3.65 (m, 1, $H_e$, $J_{ef}$ = 4.2 Hz, $J_{de}$ = 2.2 Hz), 4.89 (s, 5, $C_5H_5$), 5.70 (m, 1, $H_c$, $J_{bc}$ = 5.6 Hz, $J_{cd}$ = 2.6 Hz), 6.32 (m, 1, $H_b$, $J_{bc}$ = 5.6 Hz, $J_{ab}$ = 2.9 Hz). Anal. Calcd for $C_{17}H_{19}O_3BF_2Fe$: C, 54.30; H, 5.10. Found: C, 54.21; H, 5.

**Crystal and Molecular Structures of Complexes 5, 5a, and 5c. Collection of X-ray Diffraction Data of 5a.** Orange crystals of **5a** were crystallized from an ether/pentane solution at −20 °C. Preliminary precession photographs indicated 2/*m* Laue symmetry and revealed systematic absences along 0*k*0 for *k* odd and on *h*0*l* for *l* odd which identified the space group as $P2_1/c$. Cell parameters were determined by a least-squares fit of $2\theta$, $\omega$, and $\chi$ diffractometer settings for 15 reflections in the range $40 < 2\theta < 45°$ as measured at both $\pm 2\theta$ and Mo K$\beta_1$ radiation ($\lambda$ = 0.63225 Å). Unit cell values for *a*, *b*, *c*, and $\beta$, respectively, at 20 °C are 9.401 (3), 7.154 (3), and 25.894 (11) Å and 94.44 (2)°. The calculated cell volume is 1736 Å$^3$. With *Z* = 4 and a molecular weight of 378.01, the calculated density is 1.446 g cm$^{-3}$.

Intensity data were collected from a crystal whose dimensions were 1.0 mm × 0.2 mm × 0.5 mm. The crystal was mounted with the longest dimension parallel to the $\phi$ axis of the four-circle automated Picker

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(12) Moffett, R. B. "Organic Syntheses"; John Wiley and Sons: New York, 1963; Collect. Vol. IV, p 238.

diffractomer. The control software used for the Picker FACS-I system has been reported previously.[13] A total of 8825 reflections were measured ($\pm h$, $\pm k$, $\pm l$ for $0° \leq 2\theta \leq 15°$ and $\pm hkl$ and $\pm h,-k,-l$ for $15 < 2\theta \leq 55°$) using Mo K$\alpha$ radiation and $\theta$–$2\theta$ step scans. The step size was 0.05° with a scan width of 1.15° $2\theta$ plus a dispersion term; each step was counted for 1 s, and the background was counted for 10 s at each end of each scan. A 0.002 in niobium filter was used below 15° and a 0.001 in niobium filter was used above 15°. Absorption corrections were calculated with ORABS[14] by using a linear absorption coefficient of 8.97 $cm^{-1}$ and a Gaussian grid of $8 \times 8 \times 8$; maximum, minimum, and average transmission factors were 0.852, 0.559, and 0.772. Symmetry-related reflections were averaged to give 3988 independent structure factors.

**Solution and Refinement of the Diffraction Data of 5a.** The Fe position was determined by means of a sharpened Patterson function, and the phases provided by the Fe atom were used for difference syntheses which revealed the positions of the remaining atoms. After preliminary least-squares refinement, all the hydrogen atoms were located from a difference synthesis.

A final refinement was carried out with all the heavy atoms having anisotropic temperature factors and the hydrogen atoms having isotropic temperature factors. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F_o)^2$. The variance, $\sigma^2$, was based on counting statistics and included the usual instability term (4.0% in this case). Atomic scattering factors were those tabulated by Cromer and Mann[15] except for hydrogen where Stewart's values were used.[16] The anomalous dispersion factors used for all atoms except hydrogen were those given by Cromer and Liberman.[17] By using all reflections, the final $R$ factor calculated was 0.050; the weighted $R$ factor, $R_w = \{[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]\}^{1/2}$, was 0.046. The average and maximum shift-to-error ratios for the final refinement cycle were 0.0057 and 0.0711; the standard error of an observation of unit weight was 1.9. The maximum and minimum electron densities on the final difference map were 0.54 and −0.42 e Å$^{-3}$, both near the Fe atom. A complete listing of the final atomic positional parameters is given in Table I. The values shown were used before rounding to calculate the final structure factors.

Structure factor, electron density, and bond distance and angle calculations were performed with the X-RAY 67 programs as implemented and updated on the Vanderbilt DEC-10 computer.[18]

**Structural Determinations of Complexes 5 and 5c.** The single-crystal, X-ray diffraction structural determinations of compounds **5** and **5c** were performed analogously to that described above for complex **5a**. A summary of the crystallographic data for each compound is footnoted below.[19,20] Complete reports of these structural determinations will be published elsewhere.[21]

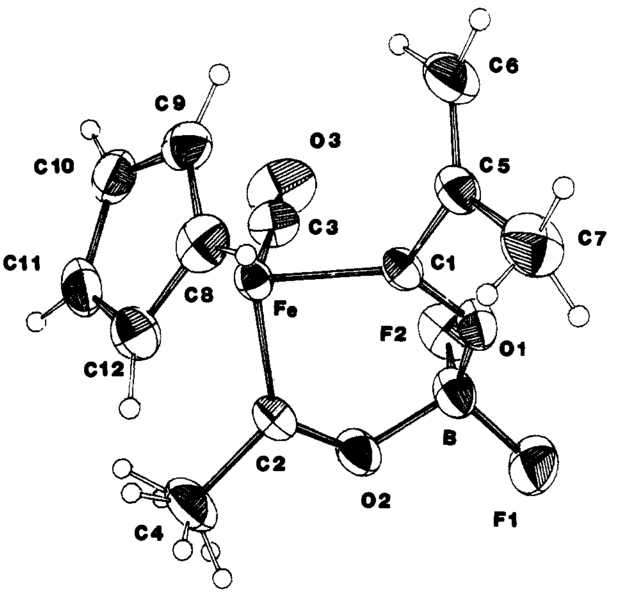
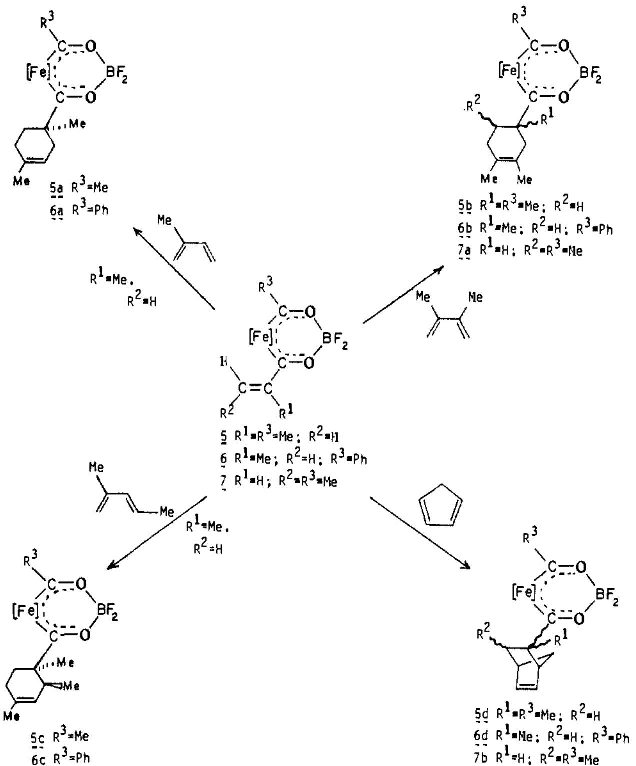


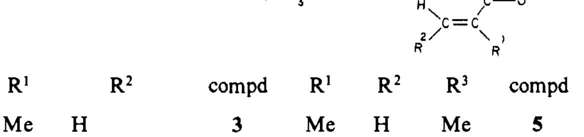
Figure 1. An ORTEP view of complex **5** (thermal ellipsoids at 30% probability).

**Scheme I.** Diels–Alder Cycloaddition Reactions of Complexes **5–7** with Selected Dienes; [Fe] = ($\eta$-$C_5H_5$)(OC)Fe



## Results

The methacrylate and crotonate derivatives of (ferra-$\beta$-diketonato)$BF_2$ complexes **5–7** are prepared from the corresponding iron methacryloyl and crotonyl complexes **3** and **4**, as shown in eq 1. Compounds **5–7** are isolated as pure solids (**5** and **7**) or



$$(\eta\text{-}C_5H_5)(OC)_2Fe{-}\overset{\overset{O}{\|}}{C}{-}C(R^1){=}C(H)(R^2) \xrightarrow[(2)\ BF_3]{(1)\ R^3Li} \quad (1)$$

| $R^1$ | $R^2$ | compd | $R^1$ | $R^2$ | $R^3$ | compd |
|---|---|---|---|---|---|---|
| Me | H | **3** | Me | H | Me | **5** |
| H | Me (trans) | **4** | Me | H | Ph | 6 |
|  |  |  | H | Me | Me | 7 |

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(13) Lenhert, P. G. *J. Appl. Crystallogr.* **1975**, *8*, 568–570.

(14) Wehe, D. J.; Busing, W. R.; Lenz, H. A. "ORABS, A Fortran Program for Calculating Single-Crystal Absorption Corrections", Report ORNL-TM-229; Oak Ridge National Laboratory: Oak Ridge, TN, 1962.

(15) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321–324.

(16) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

(17) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.

(18) Stewart, J. M. "X-RAY 67 Program System for X-ray Crystallography for the Univac 1108, CDC 3600/6600, IBM 360/50, 65, 75, IBM 7094", Technical Report TR-67-58; Computer Science Center, University of Maryland: College Park, MD, 1967.

(19) Crystallographic data for complex **5** are the following: space group $P2_1/c$ with $a$ = 7.8219 (9) Å, $b$ = 11.7939 (19) Å, $c$ = 15.4383 (19) Å, $\beta$ = 111.58 (1)° ($\lambda$ = 0.63225 Å), and $Z$ = 4. Data were collected on a yellow-orange crystal measuring ca. 0.9 mm × 0.2 mm × 0.5 mm on a four-circle automated Picker diffractomer by using Mo K$\alpha$ radiation. Data were acquired by $2\theta$ step scans out to 60° in $2\theta$. A total of 9537 reflections were measured; symmetry-related reflections were averaged to give 3863 independent structure factors. An absorption correction was applied to the data. The structure was solved by the Patterson heavy-atom method and full-matrix least-squares refinement gave $R$ = 0.042 and $R_w$ = 0.041. All atoms were refined except the hydrogen atoms on C(4). These hydrogen atoms were treated as six half-hydrogens 60° apart and were not refined.

(20) Crystallographic data for complex **5c** are the following: space group $P2_1/c$ with $a$ = 7.1611 (11) Å, $b$ = 16.8499 (27) Å, $c$ = 16.2298 (23) Å, $\beta$ = 111.76 (2)° ($\lambda$ = 0.71070 Å) and $Z$ = 4. Data were collected on a yellow-orange crystal measuring ca. 0.4 mm × 0.4 mm × 0.2 mm on a four-circle automated Picker diffractomer by using Mo K$\alpha$ radiation. Data were acquired by $2\theta$ step scans out to 55° in $2\theta$. A total of 10 166 reflections were measured; symmetry-related reflections were averaged to give 4172 independent structure factors. An absorption correction was applied to the data. The structure was solved by the Patterson heavy-atom method and final full-matrix least-squares refinement gave $R$ = 0.050 and $R_w$ = 0.045. All atoms were refined.

(21) Lenhert, P. G.; Lukehart, C. M.; Sacksteder, L. A. *Acta Crystallogr.*, submitted for publication.

**Table I.** Final Positional Parameters for Complex **5a** in Fractional Coordinates (with esd's)

| atom[a] | *x* | *y* | *z* | atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Fe | 0.28931 (3) | 0.44685 (4) | 0.34234 (1) | C(17) | 0.2404 (5) | 0.1636 (9) | 0.6156 (2) |
| F(1) | −0.0285 (2) | 0.1880 (2) | 0.30157 (6) | H(41) | 0.132 (4) | 0.843 (5) | 0.344 (2) |
| F(2) | −0.1695 (2) | 0.3187 (3) | 0.35748 (7) | H(42) | 0.205 (4) | 0.818 (5) | 0.297 (2) |
| O(1) | 0.0643 (2) | 0.2653 (3) | 0.38535 (6) | H(43) | 0.028 (4) | 0.815 (5) | 0.294 (2) |
| O(2) | −0.0050 (2) | 0.5077 (3) | 0.32250 (7) | H(61) | 0.210 (3) | −0.011 (4) | 0.444 (2) |
| O(3) | 0.4087 (2) | 0.7474 (3) | 0.40706 (8) | H(62) | 0.084 (3) | 0.098 (4) | 0.462 (1) |
| B | −0.063 (3) | 0.3147 (4) | 0.3402 (1) | H(71) | 0.461 (3) | 0.372 (4) | 0.443 (2) |
| C(1) | 0.1950 (2) | 0.3201 (3) | 0.39348 (8) | H(72) | 0.443 (3) | 0.242 (4) | 0.490 (2) |
| C(2) | 0.1205 (3) | 0.5789 (3) | 0.32561 (8) | H(73) | 0.451 (3) | 0.155 (4) | 0.435 (2) |
| C(3) | 0.3597 (3) | 0.6251 (4) | 0.38281 (9) | H(8) | 0.198 (3) | 0.174 (4) | 0.271 (2) |
| C(4) | 0.1162 (4) | 0.7829 (4) | 0.3130 (2) | H(9) | 0.263 (4) | 0.492 (5) | 0.238 (2) |
| C(5) | 0.2517 (2) | 0.2690 (4) | 0.44893 (8) | H(10) | 0.488 (4) | 0.597 (5) | 0.284 (2) |
| C(6) | 0.1871 (3) | 0.0855 (4) | 0.4666 (1) | H(11) | 0.567 (4) | 0.325 (5) | 0.347 (2) |
| C(7) | 0.4150 (3) | 0.2559 (5) | 0.4551 (1) | H(12) | 0.397 (3) | 0.090 (4) | 0.337 (1) |
| C(8) | 0.2824 (3) | 0.2490 (4) | 0.28173 (9) | H(131) | 0.327 (4) | −0.006 (5) | 0.526 (2) |
| C(9) | 0.3164 (4) | 0.4221 (2) | 0.2620 (1) | H(132) | 0.184 (4) | −0.060 (5) | 0.535 (2) |
| C(10) | 0.4437 (4) | 0.4824 (5) | 0.2879 (2) | H(15) | 0.202 (4) | 0.463 (4) | 0.564 (2) |
| C(11) | 0.4897 (3) | 0.3406 (5) | 0.3235 (2) | H(161) | 0.243 (4) | 0.520 (5) | 0.479 (2) |
| C(12) | 0.3893 (3) | 0.1976 (4) | 0.3193 (1) | H(162) | 0.097 (4) | 0.454 (4) | 0.473 (2) |
| C(13) | 0.2315 (4) | 0.0410 (5) | 0.5229 (2) | H(171) | 0.323 (5) | 0.089 (6) | 0.622 (2) |
| C(14) | 0.2258 (3) | 0.2033 (5) | 0.55795 (9) | H(172) | 0.225 (6) | 0.274 (9) | 0.634 (3) |
| C(15) | 0.2118 (3) | 0.3761 (5) | 0.5397 (1) | H(173) | 0.171 (4) | 0.081 (5) | 0.622 (2) |
| C(16) | 0.2004 (3) | 0.4266 (4) | 0.48358 (9) | | | | |

[a] The first one or two digits of the hydrogen atom designation denotes the carbon atom to which it is bonded.

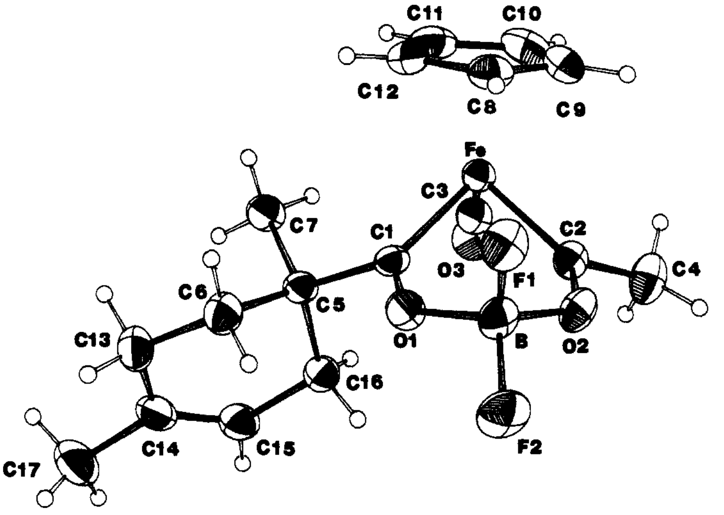

**Figure 2.** An ORTEP view of complex **5a** (thermal ellipsoids at 30% probability).

a liquid (**6**) in yields of 18–66%. The appearance of an R$^3$ methyl resonance at δ 2.86 in the $^1$H NMR spectra of **5** and **7** is a diagnostic indication of the formation of a (ferra-β-diketonato)BF$_2$ complex.[2] The carbonyl ligand C–O stretching region of the IR spectra of **5**–**7** reveals the conformation of the boat-shaped ferra-chelate ring.[22] In solution phase, all three complexes exist in both boat conformations with the major conformation being the one having an axial C$_5$H$_5$ ligand. This structure is more stable in solvents of low polarity. In the solid phase, complexes **5** and **7** adopt the boat conformation with the CO ligand in an axial position.

An X-ray structural determination of the molecular structure of **5** has been completed,[19] and an ORTEP view of this molecule is shown in Figure 1. The structural data confirm unambiguously the presence of a (ferra-β-diketonato)BF$_2$ moiety in the boat conformation having an axial CO ligand. The π-electron system of the methylacryl substituent apparently is not perturbed by the delocalized π-electron density of the ferra-chelate ring. The C(1)–C(5) and C(5)–C(6) distances are 1.500 (3) and 1.317 (3) Å, respectively, which represent normal C(sp$^2$)–C(sp$^2$) single and double bonds. The sum of the three angles about C(5) is 359.7 (2)° which indicates a planar hybridization at this atom. The two hydrogen atoms on C(6) were located and refined.

Complexes **5**–**7** react as dienophiles and undergo Diels–Alder cycloaddition reactions with isoprene, 2,3-dimethyl-1,3-butadiene (DMB), *trans*-2-methyl-1,3-pentadiene (MPD), and cyclopentadiene, as shown in Scheme I. The isoprene adduct **5a** is isolated as an amber solid in a crude yield of 82% and as a purified solid in 38% yield. The analogous compound **6a** is isolated as a deep red oil in 84% yield. Because of the chirality at the Fe and cyclohexenyl (Me)C(sp$^3$) atoms, **5a** could exist as four stereoisomers (two diastereomeric pairs of enantiomers). In addition, each diastereomer could exist as two structural isomers depending on the regiochemistry of the isoprene addition and as two conformations of the ferra-chelate ring. Infrared spectra of **5a** in solution phase and as a KBr pellet reveal that the ferra-chelate ring only adopts the boat conformation having the C$_5$H$_5$ ring in an axial position. The formation of possible structural isomers and diastereomers of **5a** has been examined by X-ray crystallography and by 400-MHz $^1$H NMR and $^{13}$C NMR.

An ORTEP view of **5a** is shown in Figure 2. A listing of the final positional parameters and selected interatomic distances and angles for **5a** are included in Tables I and II, respectively. Other structural data are provided as supplementary material. The (ferra-β-diketonato)BF$_2$ moiety has the expected structure,[3] and the ferra-chelate ring adopts the boat conformation having an axial C$_5$H$_5$ ligand as indicated by IR data. The average values of the

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[22] The assignment of the conformation of the ferra-chelate ring from IR data has been confirmed through X-ray structural determinations of *both* conformations in analogous complexes. See, ref 3 and Afzal, D.; Lenhert, P. G.; Lukehart, C. M.; Srinivasan, R. *Inorg. Chem.*, accepted for publication.

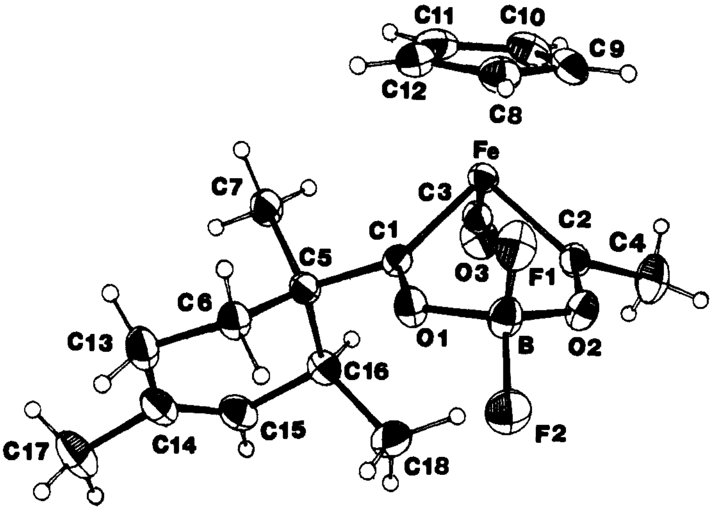

**Figure 3.** An ORTEP view of complex **5c** (thermal ellipsoids at 30% probability).

Fe–C(acyl) and C(acyl)–O distances are 1.875 and 1.287 Å, respectively. The cyclohexenyl substituent has the expected puckered-ring conformation with a C(14)–C(15) double bond distance of 1.327 (4) Å. Cycloaddition of isoprene occurs to give only the "para" structural isomer. Furthermore, only the diastereomer shown (and its enantiomer) is observed in the solid state.

Proton and $^{13}C$ NMR spectra at 400 MHz of solutions of **5a** prepared from single crystals and from the oil obtained from supernatant solutions show the same predominant diastereomer. However, the $^1H$ NMR spectrum of the sample prepared from crystalline **5a** shows *two* $C_5H_5$ singlets at $\delta$ 4.71 and 4.69 and *two* cyclohexenyl C(7) methyl singlets at $\delta$ 1.01 and 0.92. The approximate relative intensity within these pairs of singlets is 94:6, respectively. These data indicate that another minor species is present. Because complex **5b** shows the same effect (vide post), this minor isomer is presumably not due to the presence of the other structural (i.e., regio) isomer. Also, because $^1$ H NMR spectra of complex **5** at 400 MHz do not show a similar effect this minor isomer is probably not due to the presence of the other conformational isomer of the ferra-chelate ring.[23] Therefore, we tentatively assign these minor resonances to the presence of a small amount of the second diastereomer (and its enantiomer) of **5a**.

The Diels–Alder products of DMB cycloaddition, **5b** and **6b**, are isolated in crude yields of 87% and as pure solids in yields of 32 and 44%, respectively. Complex **7a** is isolated as a pure yellow solid in 8% yield. Because DMB is a symmetrical diene, only one structural (i.e., regio) isomer of the cycloaddition adduct is possible. The 400-MHz $^1H$ NMR spectra of **5b** show *two* singlets for the $C_5H_5$ resonance at $\delta$ 4.72 and 4.66 and two singlets for the cyclohexenyl C(sp$^3$)–methyl resonance at $\delta$ 0.97 and 0.92. Within each pair of singlets the relative intensities are ca. 97:3. As with complex **5a** (vide supra), these peaks are assigned to the presence of a small amount of the other diastereomer of **5b**. The structure of the major diastereomer of **5b** is assumed to be the same as that of **5a** based on the similarity of the chemical shifts of the $C_5H_5$ and cyclohexenyl C(sp$^3$)–methyl $^1H$ NMR resonances for these compounds.

A kinetic study of the reaction of **6** with DMB has been recorded under pseudo-first-order conditions in neat DMB. The reaction was followed at 33, 0, and 22.2 °C by $^1H$ NMR. The following kinetic data have been determined: $k(298\ K) = 2.86 \times 10^{-4}\ s^{-1}$; $\Delta H^{\ddagger}$ (298 K) = 8.6 (2) kcal/mol; $\Delta S^{\ddagger} = -45.7$ (2) eu.

**Table II.** Selected Interatomic Distances (Å) and Angles (deg) with Estimated Standard Deviations for Complex **5a**

| | | | |
|---|---|---|---|
| | Interatomic Distances | | |
| Fe–C(1) | 1.882 (2) | C(9)–C(10) | 1.394 (4) |
| Fe–C(2) | 1.869 (2) | C(10)–C(11) | 1.415 (5) |
| Fe–C(3) | 1.748 (2) | C(11)–C(12) | 1.390 (4) |
| Fe–C(8) | 2.111 (3) | C(8)–C(12) | 1.393 (3) |
| Fe–C(9) | 2.123 (3) | C(8)–H(8) | 0.98 (3) |
| Fe–C(10) | 2.115 (3) | C(9)–H(9) | 0.91 (4) |
| Fe–C(11) | 2.123 (3) | C(10)–H(10) | 0.93 (3) |
| Fe–C(12) | 2.122 (3) | C(11)–H(11) | 0.92 (3) |
| C(1)–O(1) | 1.292 (2) | C(12)–H(12) | 0.90 (3) |
| C(2)–O(2) | 1.282 (3) | C(15)–H(15) | 0.90 (4) |
| C(3)–O(3) | 1.152 (3) | C(6)–H(61) | 0.93 (3) |
| C(2)–C(4) | 1.495 (4) | C(6)–H(62) | 0.97 (3) |
| C(1)–C(5) | 1.537 (3) | C(13)–H(131) | 0.96 (4) |
| C(5)–C(6) | 1.531 (3) | C(13)–H(132) | 0.92 (4) |
| C(5)–C(7) | 1.535 (3) | C(16)–H(161) | 0.79 (4) |
| C(5)–C(16) | 1.541 (4) | C(16)–H(162) | 1.01 (3) |
| C(6)–C(13) | 1.518 (4) | C(4)–H(41) | 0.91 (4) |
| C(13)–C(14) | 1.478 (4) | C(4)–H(42) | 1.00 (4) |
| C(14)–C(15) | 1.327 (4) | C(4)–H(43) | 0.96 (4) |
| C(14)–C(17) | 1.515 (4) | C(7)–H(71) | 1.00 (3) |
| C(15)–C(16) | 1.492 (4) | C(7)–H(72) | 0.91 (3) |
| B–O(1) | 1.487 (3) | C(7)–H(73) | 0.96 (3) |
| B–O(2) | 1.491 (3) | C(17)–H(171) | 0.95 (4) |
| B–F(1) | 1.357 (3) | C(17)–H(172) | 0.94 (6) |
| B–F(2) | 1.362 (3) | C(17)–H(173) | 0.91 (4) |
| C(8)–C(9) | 1.387 (4) | | |
| | Interatomic Angles | | |
| Fe–C(1)–O(1) | 121.7 (2) | C(12)–C(8)–C(9) | 108.6 (3) |
| Fe–C(2)–O(2) | 125.1 (2) | C(1)–C(5)–C(7) | 112.5 (2) |
| Fe–C(3)–O(3) | 176.2 (3) | C(1)–C(5)–C(6) | 111.5 (2) |
| Fe–C(2)–C(4) | 123.5 (2) | C(1)–C(5)–C(16) | 105.6 (2) |
| Fe–C(1)–C(5) | 128.6 (2) | C(7)–C(5)–C(6) | 109.5 (2) |
| C(1)–Fe–C(2) | 88.20 (9) | C(7)–C(5)–C(16) | 109.9 (2) |
| C(1)–Fe–C(3) | 96.1 (1) | C(6)–C(5)–C(16) | 107.7 (2) |
| C(2)–Fe–C(3) | 92.6 (1) | C(5)–C(16)–C(15) | 112.8 (2) |
| C(4)–C(2)–O(2) | 111.4 (3) | C(16)–C(15)–C(14) | 124.8 (3) |
| C(5)–C(1)–O(1) | 109.7 (2) | C(15)–C(14)–C(13) | 121.3 (3) |
| O(1)–B–O(2) | 109.5 (2) | C(15)–C(14)–C(17) | 121.7 (4) |
| F(1)–B–F(2) | 111.1 (2) | C(17)–C(14)–C(13) | 117.0 (4) |
| C(8)–C(9)–C(10) | 108.2 (3) | C(14)–C(13)–C(6) | 113.9 (3) |
| C(9)–C(10)–C(11) | 107.4 (3) | C(13)–C(6)–C(5) | 112.4 (3) |
| C(10)–C(11)–C(12) | 107.8 (3) | C(14)–C(15)–H(15) | 114 (2) |
| C(11)–C(12)–C(8) | 108.0 (3) | C(16)–C(15)–H(15) | 121 (2) |
| C(1)–O(1)–B | 126.5 (2) | C(2)–O(2)–B | 123.4 (2) |

Complex **7a** is formed presumably with retention of the trans stereochemistry of the dienophile. However, direct confirmation of this structure from the $^1H$ NMR spectra is precluded by the extensive coupling and broadened resonances observed for this compound.

The MPD cycloaddition products **5c** and **6c** are isolated in crude yields of 75% and as pure solids in yields of 26–34%. An X-ray structural determination of **5c** has been performed,[20,21] and an ORTEP view of the molecule is shown in Figure 3. The (ferra-$\beta$-diketonato)$BF_2$ moiety has the expected structure,[3] and the

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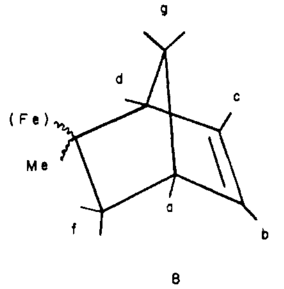
[23] The conformational isomers of the ferra-chelate ring apparently interconvert rapidly on the NMR time scale at ambient probe temperature at both 100 and 400 MHz. We also assume that the cyclohexenyl ring conformational isomers are not observed as distinct species on the NMR time scale.

ferra-chelate ring adopts the boat conformation with the $C_5H_5$ ligand in an axial position. The average values of the Fe–C(acyl) and C(acyl)–O distances are 1.873 and 1.293 Å, respectively. The cyclohexenyl substituent has the expected puckered-ring conformation with a C(14)–C(15) double bond distance of 1.318 (4) Å. Cycloaddition of MPD occurs to give the "ortho, para" structural isomer. Furthermore, only the diastereomer shown and its enantiomer are observed in the solid state. The configurations about C(5) in structures **5a** and **5c** are the same.

The 400-MHz $^1$H NMR spectra of bulk solutions of **5c** reveal additional resonances for the $C_5H_5$, the acetyl methyl, and the sp$^3$-C(7) methyl groups. For the $C_5H_5$ group, three additional singlets are observed at δ 4.71, 4.69, and 4.66. The largest resolved additional resonance at δ 4.71 has a relative intensity of 6:94 compared to the principal $C_5H_5$ resonance at δ 4.68. We tentatively assign these additional resonances to minor abundances of three additional diastereomers of **5c**. The resonances of the acetyl methyl group indicate a presence of only three species.

The structure of **6c** is assumed to be analogous to that of **5c**, although extensive specific structural data have not been obtained.

The cyclopentadiene Diels–Alder products **5d**, **6d**, and **7b**, are isolated as pure complexes in yields of 49–98%. Cycloaddition gives either endo or exo isomers defined by the relative orientation of the Fe moiety and the norbornenyl fragment. Isomer assignment is readily discerned from the $^1$H NMR spectral data (see **8** and **9**). For exo isomers, the proton resonances for the b and c protons appear as a broad singlet, while for endo isomers these protons give separated multiplet resonances.[24]



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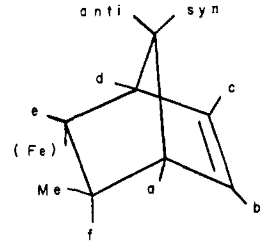

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Complex **5d** is isolated as an ca. 1:1 mixture of endo/exo isomers **8**. The endo isomer can be crystallized as a pure yellow solid. Complex **6d** is isolated as a solid having an ca. 45:55 endo/exo isomer ratio (see **8**). Complex **7b** is obtained as only the endo isomer **9**. The diastereomeric purity of complexes **5d**, **6d**, and **7b** has not been determined from high-field NMR spectral data.

## Discussion

A diagnostic indication of the formation of these Diels–Alder cycloaddition products is revealed in the $^1$H NMR spectra. In going from the reactant complexes **5**, **6**, or **7** to the Diels–Alder adducts, the methyl resonance of the methacryl or crotonyl substituent at δ 1.85–1.97 shifts significantly to much higher field, δ 0.75–1.06, as this methyl group becomes the C(7)-methyl substituent of the cyclohexenyl group.

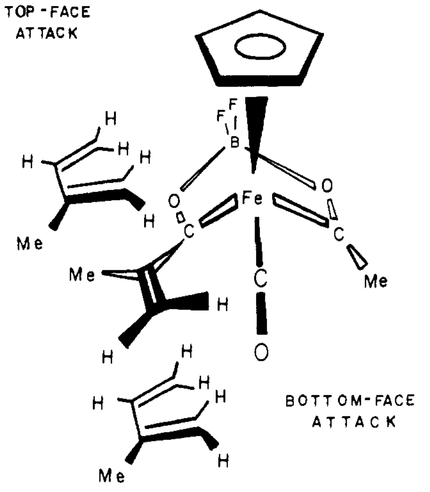
Solution IR data reveal that these reactant and product complexes exist as ferra-chelate ring boat conformations having the $C_5H_5$ ligands in axial sites. This conformation is preferred when the ferra-chelate ring substituents are sterically bulky groups.[22] Complex **7a** apparently violates this general rule, however. In the solid state, complexes **5** and **7** prefer the opposite ferra-chelate ring boat conformation presumably due to more favorable intermolecular interactions within the lattice.

The rate of reaction of **6** with DMB is ca. 50 times greater than the rate of reaction of DMB with methyl methacrylate under similar reaction conditions.[25] This rate enhancement confirms the anticipated activation of the dienophile by the ferra moiety including the Lewis acid effect of the $BF_2$ group. The (ferra-β-diketonato)$BF_2$ moiety apparently activates dienophiles toward Diels–Alder cycloadditions similar to the analogous activation of dienophile groups by group VI alkenyl carbene complexes.[26] The large negative value of $\Delta S^*$ for the reaction of **6** with DMB is consistent with a bimolecular cycloaddition mechanism.[10]

Regarding the regiochemistry of these Diels–Alder reactions, the formation of **5a** obeys the "para" rule, and the formation of **5c** obeys the "ortho, para" rule. In each reaction, the formation of the other regioisomer is not evident. These results are consistent with those reported for uncatalyzed reactions of methyl methacrylate.[27] Methyl methacrylate reacts with isoprene at 220 °C to give a "para"/"meta" isomer ratio of 9:1, and it reacts with MPD to give the "ortho, para" isomer in greater than 95% relative abundance compared to the relative abundance of the "meta, meta" structural isomer. This observed regioselectivity presumably results from frontier control of the reaction mechanism.[10]

Regarding the stereochemistry of these Diels–Alder reactions, complexes **5a**, **5b**, and **5c** are formed with very high apparent stereoselectivity as the *same* diastereomer at the Fe and C(5) centers. In addition, **5c** has a chiral center at C(16), and this complex is formed predominantly with only the relative configuration at C(5) and C(16) shown in Figure 3. Such stereospecificity requires that during the approach of the dienes and dienophiles the adduct formation discriminates between the two sides (or faces) of the dienophiles. Because this stereospecificity results from a kinetically-controlled process, a structural definition of the transition state structure must be formulated to rationalize these observations. Following the Prelog–Cram stereochemical model as applied by Walborsky et al., to asymmetric Diels–Alder reactions,[28] the transition-state structure of the dienophile can be defined tentatively.

By using this method, a stereochemical analysis of the Diels–Alder additions to complex **5** would proceed in the following manner. A model of the solid-state structure of **5**, see Figure 1, is first converted into the solution-state species by "flipping" the ferra-chelate ring to the other boat isomer having an axial $C_5H_5$ ligand. Next, the appropriate conformation of the methacrylate ligand is chosen to be the one having the C–C double bond *transoid* to the ferra-chelate ring C–O multiple bond in which the atoms C(1), O(1), C(5), and C(6) are coplanar. Molecular models reveal that the dienophile now has a "top" face defined by the proximity of the axial $C_5H_5$ ligand and a "bottom" face defined by the proximity of the equatorial CO ligand (see **10**).



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Approach of a 1,3-diene (in a parallel plane orthogonal to the direction of $\sigma$ bond formation) to the "bottom" face of the dienophile is restricted due to unfavorable H(diene)···O(CO ligand) interactions. Approach of a 1,3-diene to the "top" face appears to be more favorable. This approach of isoprene generates the proper diastereomers of **5a**.[29] Approach of isoprene from the "bottom" face of the dienophile generates the unobserved (or minor) diastereomers of **5a**. A similar "top-face" approach of DMB and MPD affords the correct diastereomers of **5b** and **5c**, also (including the relative stereochemistry at C(5) and C(16) of **5c**, see Figure 3). The unusually high stereospecificity of these Diels–Alder reactions might also be related to the rigid conformation of the $BF_2$ coordination to the carbonyl oxygen atom of the dienophile imposed by the chelating ferra-$\beta$-diketonato ligand.[28,30]

The formation of a mixture of endo and exo isomers of **5d** and **6d** and of predominantly the endo isomer of **7b** is not unusual. The "endo" rule is frequently violated for reactions of methyl methacrylate with cyclopentadiene under both catalyzed or noncatalyzed conditions.[31] A wide range of endo/exo isomer ratios is observed in these analogous organic reactions. Both endo and exo isomers can be formed from "top-side" approach of cyclopentadiene on the appropriate (ferra-$\beta$-diketonato)$BF_2$ complex.

## Conclusions

(Ferra-$\beta$-diketonato)$BF_2$ complexes having alkenyl substituents on the ferra-chelate ring react as activated dienophiles in Diels–Alder cycloaddition reactions. In this study, ten such Diels–Alder adducts have been prepared and characterized. The regioselectivity of these cycloadditions is very high and follows the regiochemistry exhibited by methyl methacrylate in analogous Diels–Alder reactions. Furthermore, due to the highly asymmetric Fe moiety within the methacrylate dienophile, diene cycloaddition occurs with unusually high stereoselectivity when diastereomeric adducts are formed. We hope to apply this stereoselectivity to the synthesis of more complex organic molecules.

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**Supplementary Material Available:** A complete listing of final atomic positional and thermal parameters (before rounding) and final observed and calculated structure factors for **5a** (23 pages). Ordering information is given on any current masthead page.

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(29) Actually, this approach of isoprene generates the mirror image of **5a** as shown in Figure 2. By using the mirror image of **5**, this approach of isoprene generates the enantiomer of **5a** shown in Figure 2. Both enantiomeric diastereomers of **5a** are present in this centrosymmetric lattice.

(30) Molecular models reveal that the observed diastereomers can be formed also from the appropriate "bottom-face" approach of the dienes to the *cisoid* conformation of the dienophiles. The relative stabilities of the *cisoid* and *transoid* conformations of the dienophiles is not known. However, the *cisoid* conformation of **5** places the $C_5H_5$ ligand into closer proximity to the methacryl methyl substituent than does the *transoid* conformation, so the *transoid* conformation might be expected to be more stable.

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# Intramolecular Photocycloadditions–Cyclobutane Fragmentation: Total Synthesis of (±)-Pentalenene, (±)-Pentalenic Acid, and (±)-Deoxypentalenic Acid

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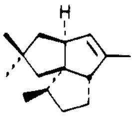
**Abstract:** Pentalenene, pentalenic acid, and deoxypentalenic acid, important metabolites in the biosynthesis of the pentalenolactones, have been synthesized from methyl isobutyrate through a common intermediate. The initial key step involves a novel conjugate addition–cycloacylation sequence on an acetylenic diester. The 1,6-diene which results is converted in two steps to a 1,6-diene diester which undergoes a highly stereoselective photocycloaddition to set three of the necessary stereocenters. Reductive cleavage of one cyclobutane bond produces a functionalized spirobicyclo[4.4]nonanone which is converted in three steps to dione **10**, the pivotal intermediate. Differential functionalization of this system provides efficient, stereocontrolled routes to pentalenene, pentalenic acid, and deoxypentalenic acid, all in racemic form.

Pentalenene (**1**),[1,2] pentalenic acid (**2**),[3,4] and deoxypentalenic acid glucuron (**3a**)[5] are members of a larger class of metabolites which contain the tricyclo[6.3.0.0$^{4,8}$]undecane skeleton. This group of angularly fused triquinanes includes the sesquiterpenes isocomene (**4**),[6,7] silphinene (**5**),[8,9] and 5-oxosilphiperfolene (**6**),[10,11]



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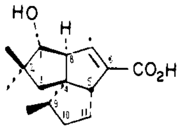

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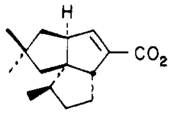
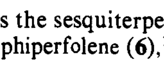


3a R =



3b R = H

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