

also be considered to be present in the title compound, which is in good agreement with the observed ligand-field spectrum (solid-state reflectance electronic spectrum in the visible and near infrared) of this compound (Blonk *et al.*, 1985).

Spectroscopic data could not predict that the aniline N would take part in the coordination (Blonk *et al.*, 1985). However, the aniline N is clearly coordinated to the Co ion. Thus the angles around the aniline N do not diverge greatly from ideal tetrahedral values (see Table 2). In [CuBr₂(pabd)] the aniline N is also coordinated (Blonk *et al.*, 1985). On the other hand, in [CoCl₂(pabd)] the aniline N is not coordinated to the Co ion (Blonk *et al.*, 1985). In similar complexes, with a nitroxyl spin label in place of the aniline, the metal–nitroxyl electron–electron exchange interaction has been found to be dependent on solvent, temperature and the presence or absence of methyl substituents on the pyrazole rings. These data suggest that the strength of the metal bond to the central N of the ligand may vary substantially from one complex to another (Eaton & Eaton, 1986). The phenyl ring and the pyrazole rings are planar (distances to the least-squares planes less than 0.015 Å) and the methyl C atoms are coplanar with the respective pyrazole rings (distances to the least-squares planes less than 0.08 Å). The pyrazole rings are neither

coplanar with the phenyl ring [interplanar angles 74.8 (3) and 161.3 (3)°] nor mutually coplanar [116.5 (3)°].

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Reactions of Coordinated Molecules. 44. Structure of a Diels–Alder Adduct of an Organometallic Dienophile

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Abstract. Difluoro[1-(1,2,4-trimethylcyclohex-3-en-1-yl)-2-(carbonylcyclopentadienylferra)butene-1,3-dionato-*O,O'*]boron, $(\eta\text{-C}_5\text{H}_5)(\text{OC})\text{Fe}(\text{MeCO})\text{-}[\{\text{CH}_2\text{CH}_2(\text{Me})\text{C}(\text{Me})\text{C}(\text{O})\text{CO}\}]_2\text{BF}_2$, $M_r = 392.04$, monoclinic, $P2_1/c$, $a = 7.161(1)$, $b = 16.850(3)$, $c = 16.230(3)$ Å, $\beta = 111.77(2)^\circ$, $V = 1818.72$ Å³, $Z = 4$, $D_x = 1.432$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 8.59$ cm⁻¹, $F(000) = 816$, $T = 294$ K. Final $R = 0.050$ for 4172 observed reflections. The structure of the substituted cyclohexene formed by cycloaddition of *trans*-2-methyl-1,3-pentadiene to a methacryl (ferra- β -diketonato)BF₂ complex confirms the regiochemistry and the stereochemistry of the

Diels–Alder reaction. The ‘*ortho*, *para*’ regioisomer is formed, and the highly stereoselective formation of one diastereomer is established. The ferra- β -diketonato substituent adopts a boat-shaped conformation having the cyclopentadienyl ligand in an axial position.

Introduction. When the complex $(\eta\text{-C}_5\text{H}_5)(\text{OC})\text{Fe}(\text{MeCO})[(\text{methacryl})\text{CO}]_2\text{BF}_2$ (Lenhert, Lukehart & Sacksteder, 1986*b*) is treated with isoprene, 2,3-dimethyl-1,3-butadiene, *trans*-2-methyl-1,3-pentadiene and cyclopentadiene, it reacts as an activated dienophile to give Diels–Alder cycloaddition products. These adducts are formed with high regio- and stereoselectivity (Lenhert, Lukehart & Sacksteder, 1986*a*). It is apparent from 400 MHz ¹H NMR data of the

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cycloaddition product obtained from the *trans*-2-methyl-1,3-pentadiene reaction that the four expected diastereomers are formed; however, one diastereomer is formed in much higher yield affording a stereoselectivity of >90%. The molecular structure of this major species is reported herein to confirm unambiguously the regio- and stereoselectivity of this adduct formation, and to facilitate future structural assignments based solely on NMR data.

Experimental. The above complex, prepared as described elsewhere (Lenhert *et al.*, 1986b), was crystallized from an ether/pentane solution at 253 K as yellow-orange crystals. Laue symmetry ($2/m$) and systematic absences (k odd $0k0$ and l odd $h0l$) on precession photographs require space group to be $P2_1/c$. Reported cell parameters are from a least-squares fit of 2θ , ω and χ for 15 reflections ($48 < 2\theta < 52^\circ$) measured at $\pm 2\theta$ with unresolved Mo $K\alpha$ radiation. [The mosaic spread of the crystal (*ca* 0.2° FWHM) and the instrumental parameters used account for the failure to resolve the α doublet.] A crystal, $0.4 \times 0.4 \times 0.2$ mm, was mounted with one of the longer dimensions parallel to the diffractometer ϕ axis. The Picker FACS-I software (Lenhert, 1975) was used to measure θ - 2θ step scans to $\sin\theta/\lambda$ of 0.65 \AA^{-1} with Mo $K\alpha$ radiation from a graphite monochromator. For the 10166 reflections measured ($\pm h \pm k \pm l$, $0-25^\circ$; $\pm h k l$ and $\pm h -k -l$, $25-55^\circ$), conditions were: 0.05° 2θ step; scan width of 1.15° plus dispersion; 10 s backgrounds at scan ends; coincidence-loss correction. Five monitor reflections measured at intervals were used to correct the intensity decrease which accumulated to 12%. Absorption was corrected with *ORABS* (Wehe, Busing & Levy, 1962) using an $8 \times 8 \times 8$ Gaussian grid; maximum, minimum and average transmission factors were 0.84, 0.76 and 0.80. Symmetry-related reflections were averaged to give 4172 independent F_o , all (including 202 with zero intensity) were used in the refinement.

The Fe position was taken from a sharpened Patterson function, and the remaining atoms were located on difference syntheses. After preliminary refinement, H atoms were located from a difference synthesis. Refinement was by full-matrix least squares; heavy atoms, anisotropic, H atoms, isotropic. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F_o)$. The variance, σ^2 , based on counting statistics included the usual instability term (4.0%). Atomic scattering factors were from Cromer & Mann (1968) except for H values (Stewart, Davidson & Simpson, 1965). Anomalous-dispersion factors were those of Cromer & Liberman (1970). The final R (all reflections) was 0.050; $wR = 0.045$. The maximum shift-to-e.s.d. for the final refinement cycle was 0.18, $S = 2.0$, maximum and minimum $\Delta\rho$ values were 0.61 and -0.20 e \AA^{-3} , both near the Fe atom. Atomic

parameters are listed in Table 1, and interatomic distances and angles are listed in Table 2.* An *ORTEP* view (Johnson, 1976) of the molecular structure including the atomic-numbering scheme is shown in Fig. 1. Structure-factor, electron-density and bond distance and angle calculations were performed with the *XRAY67* programs (Stewart, 1967) as implemented and updated on the Vanderbilt DEC-10 computer.

* Lists of anisotropic thermal parameters before rounding, non-essential bond distances and angles, selected least-squares-planes' and dihedral-angle data, and final observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43553 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and B or B_{eq} thermal parameters (\AA^2)

$B_{eq} = \frac{2}{3}\pi^2(U_{11}^2 + U_{22}^2 + U_{33}^2)$ were the U_{ii} are the r.m.s. principal-axis deviations.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> or B_{eq}
Fe	0.80445 (4)	-0.03439 (2)	0.22219 (2)	2.80
F(1)	0.94545 (19)	0.07600 (9)	0.06058 (8)	4.66
F(2)	0.84001 (22)	0.19516 (8)	0.09135 (9)	5.14
O(1)	0.98450 (21)	0.10888 (8)	0.20743 (9)	3.43
O(2)	0.65301 (21)	0.08498 (9)	0.09343 (9)	3.54
O(3)	0.58700 (26)	-0.03048 (10)	0.34119 (11)	4.72
B	0.85874 (39)	0.11588 (16)	0.11019 (17)	3.58
C(1)	0.96441 (28)	0.05719 (11)	0.26228 (13)	2.77
C(2)	0.61409 (30)	0.02846 (12)	0.13859 (13)	3.16
C(3)	0.67847 (31)	-0.02949 (12)	0.29629 (14)	3.32
C(4)	0.39138 (38)	0.01880 (22)	0.11296 (23)	5.05
C(5)	1.08493 (30)	0.08276 (11)	0.35896 (13)	2.96
C(6)	1.26437 (34)	0.13479 (14)	0.36399 (15)	3.61
C(7)	1.15980 (43)	0.00963 (15)	0.41925 (16)	4.04
C(8)	0.93949 (39)	-0.08961 (15)	-0.14014 (17)	4.13
C(9)	0.74982 (44)	-0.12463 (14)	0.12436 (18)	4.51
C(10)	0.75269 (47)	-0.15817 (14)	0.20328 (18)	4.70
C(11)	0.94440 (47)	-0.14574 (14)	0.26901 (18)	4.83
C(12)	1.05910 (42)	-0.10340 (15)	0.22973 (19)	4.58
C(13)	1.38526 (38)	0.16182 (17)	0.45935 (17)	4.43
C(14)	1.25423 (40)	0.19160 (13)	0.50562 (15)	4.20
C(15)	1.05971 (41)	0.17678 (14)	0.47504 (16)	4.25
C(16)	0.93986 (34)	0.13121 (14)	0.39193 (15)	3.65
C(17)	1.35897 (63)	0.23750 (21)	0.59103 (20)	5.86
C(18)	0.79509 (47)	0.18675 (17)	0.32455 (21)	4.88
H(41)	0.3595 (44)	-0.0366 (18)	0.1195 (21)	7.6 (9)
H(42)	0.3665 (54)	0.0408 (20)	0.1603 (25)	10.7 (12)
H(43)	0.3145 (52)	0.0383 (18)	0.0572 (24)	9.5 (10)
H(61)	1.3515 (33)	0.1055 (12)	0.3375 (14)	3.9 (5)
H(62)	1.2129 (29)	0.1812 (12)	0.3245 (14)	3.3 (4)
H(71)	1.2788 (43)	-0.0219 (16)	0.4065 (18)	7.5 (8)
H(72)	1.2188 (36)	0.0263 (13)	0.4804 (17)	5.1 (6)
H(73)	1.0452 (41)	-0.0268 (15)	0.4176 (17)	6.0 (7)
H(8)	0.9794 (36)	-0.0616 (14)	0.1009 (15)	4.5 (6)
H(9)	0.6482 (36)	-0.1215 (13)	0.0709 (16)	4.9 (6)
H(10)	0.6377 (38)	-0.1838 (14)	0.2097 (16)	5.6 (6)
H(11)	1.0040 (36)	-0.1617 (14)	0.3320 (16)	5.6 (6)
H(12)	1.1874 (35)	-0.0844 (15)	0.2580 (15)	5.0 (6)
H(131)	1.4793 (33)	0.2040 (13)	0.4549 (14)	4.4 (5)
H(132)	1.4621 (36)	0.1179 (14)	0.4935 (16)	5.0 (6)
H(15)	0.9771 (33)	0.1981 (12)	0.5035 (14)	4.1 (5)
H(16)	0.8490 (31)	0.0908 (12)	0.4055 (13)	3.8 (5)
H(171)	1.4429 (43)	0.2795 (18)	0.5816 (18)	7.5 (8)
H(172)	1.2596 (47)	0.2579 (19)	0.6162 (21)	8.8 (10)
H(173)	1.4641 (46)	0.2044 (18)	0.6301 (21)	7.8 (9)
H(181)	0.7223 (36)	0.2149 (14)	0.3566 (16)	5.4 (6)
H(182)	0.8819 (42)	0.2254 (16)	0.3082 (18)	7.2 (8)
H(183)	0.6805 (42)	0.1585 (18)	0.2726 (18)	7.6 (8)

Discussion. The structure of the substituted cyclohexene ring establishes the regiochemistry of the Diels–Alder cycloaddition of the asymmetrical diene [which is defined by C(13), C(14), C(15) and C(16) along with the C(17) and C(18) methyl substituents]. Location of the terminal C(18) methyl group of the original diene on a C atom ‘ortho’ to C(5) and the internal C(17) methyl group on a C atom ‘para’ to C(5) confirms the formation of the ‘ortho, para’ regioisomer of the adduct. Formation of this structural isomer is

kinetically preferred over the alternate ‘meta, meta’ regioisomer on the basis of frontier-controlled attack by the diene on the dienophile (Sauer & Sustmann, 1980). The C(14)–C(15) distance of 1.318 (4) Å is typical of a C(sp²)–C(sp²) double bond. The *trans* or *anti* relative orientation of the C(7) and C(18) methyl groups is consistent with a concerted mechanism for the Diels–Alder addition reaction whereby the diene and the dienophile approach one another in parallel planes perpendicular to the direction of the two C–C σ bonds which are being formed.

Table 2. Selected bond distances (Å) and angles (°)

Fe–C(1)	1.888 (2)	C(6)–C(13)	1.536 (3)
Fe–C(2)	1.857 (2)	C(13)–C(14)	1.490 (4)
Fe–C(3)	1.753 (3)	C(14)–C(15)	1.318 (4)
Fe–C(8)	2.128 (3)	C(14)–C(17)	1.520 (4)
Fe–C(9)	2.127 (3)	C(15)–C(16)	1.512 (3)
Fe–C(10)	2.121 (2)	C(16)–C(18)	1.519 (3)
Fe–C(11)	2.130 (2)	C(8)–C(9)	1.414 (4)
Fe–C(12)	2.128 (3)	C(9)–C(10)	1.393 (4)
C(1)–O(1)	1.291 (3)	C(10)–C(11)	1.407 (4)
C(2)–O(2)	1.294 (3)	C(11)–C(12)	1.407 (5)
C(3)–O(3)	1.146 (3)	C(12)–C(8)	1.406 (3)
C(2)–C(4)	1.500 (3)	B–O(1)	1.504 (3)
C(1)–C(5)	1.545 (3)	B–O(2)	1.489 (3)
C(5)–C(6)	1.533 (3)	B–F(1)	1.362 (3)
C(5)–C(7)	1.541 (3)	B–F(2)	1.366 (3)
C(5)–C(16)	1.563 (4)		
Fe–C(1)–C(5)	128.09 (15)	C(13)–C(14)–C(15)	121.4 (2)
Fe–C(1)–O(1)	121.49 (13)	C(13)–C(14)–C(17)	116.2 (3)
O(1)–C(1)–C(5)	110.4 (2)	C(15)–C(14)–C(17)	122.4 (3)
Fe–C(2)–C(4)	123.9 (2)	C(6)–C(13)–C(14)	112.5 (2)
Fe–C(2)–O(2)	125.43 (15)	C(5)–C(6)–C(13)	111.8 (2)
O(2)–C(2)–C(4)	110.7 (2)	B–O(1)–C(1)	126.9 (2)
Fe–C(3)–O(3)	175.1 (2)	B–O(2)–C(2)	124.08 (15)
C(1)–Fe–C(2)	88.45 (8)	C(9)–C(8)–C(12)	107.1 (3)
C(1)–Fe–C(3)	97.24 (10)	C(8)–C(9)–C(10)	108.5 (2)
C(2)–Fe–C(3)	92.83 (10)	C(9)–C(10)–C(11)	108.3 (3)
C(1)–C(5)–C(6)	110.8 (2)	C(10)–C(11)–C(12)	107.5 (3)
C(1)–C(5)–C(7)	110.7 (2)	C(8)–C(12)–C(11)	108.6 (2)
C(1)–C(5)–C(16)	107.54 (15)	O(1)–B–O(2)	109.3 (2)
C(6)–C(5)–C(7)	109.6 (2)	F(1)–B–O(1)	110.8 (2)
C(6)–C(5)–C(16)	109.5 (2)	F(2)–B–O(1)	106.4 (2)
C(7)–C(5)–C(16)	108.6 (2)	F(1)–B–O(2)	110.9 (2)
C(5)–C(16)–C(15)	109.9 (2)	F(2)–B–O(2)	107.0 (2)
C(5)–C(16)–C(18)	116.0 (2)	F(1)–B–F(2)	112.2 (2)
C(15)–C(16)–C(18)	109.8 (2)		
C(14)–C(15)–C(16)	127.1 (3)		

The determination of the relative stereochemistry of the asymmetric C(5), C(16) and Fe centers defines the particular diastereomer isolated as the major product (along with its enantiomer which is also present in the crystal). Of particular interest is the relative stereochemistry at C(5) and Fe. Following the Prelog–Cram stereochemical model, as applied by Walborsky, Barash & Davis (1963) to asymmetric Diels–Alder reactions, this diastereomer is formed when the diene approaches the dienophile from the ‘top’ face. The reactive conformation of the dienophile would have the (ferra-β-diketonato)BF₂ structure as shown in Fig. 1 and a *transoid* orientation of the C(5)–C(6) double bond and the C(1)–O(1) multiple bond relative to the C(1)–C(5) bond [the atoms C(1), O(1), C(5) and C(6) would be coplanar according to this model]. Molecular models reveal that attack by the diene at the C₅H₅ or ‘top’ face of the dienophile is less restricted sterically than attack by the diene at the carbonyl ligand or ‘bottom’ face of the dienophile. The asymmetry at the Fe atom apparently controls the stereochemistry of the Diels–Alder addition.

Bond distances and angles within the (ferra-β-diketonato)BF₂ substituent are as expected based on structural data of analogous complexes (Lenhart, Lukehart & Warfield, 1980; Lenhart *et al.*, 1986*a,b*). The Fe–C(acyl) distances of 1.888 (2) and 1.857 (2) Å and the C(acyl)–O distances of 1.291 (3) and 1.294 (3) Å indicate bonds having multiple-bonding character. The ferra-chelate ring adopts a boat-shaped conformation having a C₅H₅ ligand occupying an axial site (Afzal, Lenhart, Lukehart & Srinivasan, 1986).

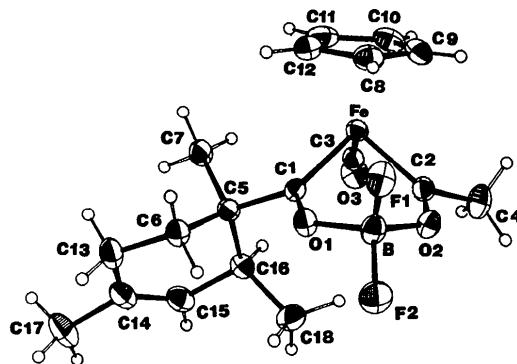


Fig. 1. An ORTEP view (ellipsoids at 30% probability) showing the atomic-numbering scheme.

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Structure of Di[3,4;3',4'-bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalenium] Dichlorocuprate(I), (BEDT-TTF)₂CuCl₂

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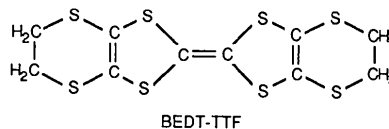
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Abstract. 2C₁₀H₈S₈^{1/2+}·CuCl₂⁻, *M_r* = 903·8, monoclinic, *P*2/*c*, *a* = 7·941 (2), *b* = 6·676 (2), *c* = 30·586 (9) Å, β = 97·47 (2)°, *V* = 1607·7 (6) Å³, *Z* = 2, *D_x* = 1·87 Mg m⁻³, λ(Mo *K*α) = 0·71073 Å, μ = 1·87 mm⁻¹, *F*(000) = 910, *T* = 298 K, *R*(*F*) = 0·049 for 1897 observed reflections. The structure consists of layers (within the *ab* plane) of partially oxidized BEDT-TTF molecules separated by isolated, linear CuCl₂⁻ anions along the *c* direction. Within the layers, transverse, or interstack intermolecular S··S contacts along the *b* direction are shorter than the intrastack distances (along *a*). The electrical conductivity is thermally activated, with *E_a* = 0·15 eV and σ_{300 K} = 0·003 (Ωcm)⁻¹.

Introduction. Superconductivity has been observed in a number of (BEDT-TTF)₂X charge-transfer salts with linear triatomic monovalent anions, including β-(BEDT-TTF)₂I₃ (*T_c* ≈ 1·5 K at ambient pressure; Yagubskii, Shchegolev, Laukhin, Kononovich, Kartsovnik, Zvarykina & Buravov, 1984; Williams, Emge, Wang, Beno, Copps, Hall, Carlson & Crabtree, 1984), β-(BEDT-TTF)₂IBr₂ (*T_c* ≈ 2·8 K, Williams, Wang, Beno, Emge, Sowa, Copps, Behroozi, Hall, Carlson & Crabtree, 1984), and β-(BEDT-TTF)₂AuI₂ (*T_c* ≈ 5 K, Wang, Beno, Geiser, Firestone, Webb,

Núñez, Crabtree, Carlson, Williams, Azevedo, Kwak & Schirber, 1985). Other BEDT-TTF salts have metallic conductivity, e.g. β-(BEDT-TTF)₂I₂Br (Emge, Wang, Beno, Leung, Firestone, Jenkins, Cook, Carlson, Williams, Venturini, Azevedo & Schirber, 1985), or behave as semiconductors, viz β-(BEDT-TTF)₂ICl₂ (Emge, Wang, Leung, Rust, Cook, Jackson, Carlson, Williams, Whangbo, Venturini, Schirber, Azevedo & Ferraro, 1986; Kobayashi, Kato, Kobayashi, Saito, Tokumoto, Anzai & Ishiguro, 1986). Anion size and symmetry are some of the factors that determine if a salt becomes a superconductor at low temperatures (Emge, Leung, Beno, Wang, Firestone, Webb, Carlson, Williams, Venturini, Azevedo & Schirber, 1986).



Most BEDT-TTF charge-transfer salts consist of layers of donor radical molecules, separated by counteranions. Within the layers, stacking is usually observed. Short intermolecular S··S contacts (compared with the van der Waals radii sum, 3·6 Å; Bondi, 1964) are involved in the electrical conduction pathways. The details of the packing, as determined in part by the cation–anion interactions, influence the electronic band structure, and thus the electrical properties.

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