

Access to Homochiral Acyclic (diene)Fe(CO)₃ Complexes Containing Electron Donor Substituents

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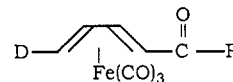
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(2,4-pentadienyl)Fe(CO)₃ complexes containing electron donor 5-substituents (OMe, OCOR, NR₂) have been prepared and resolved via oxazolidine or imine derivatives or through incorporation of a homochiral dialkylamino auxiliary. Absolute configurations have been established by X-ray crystallography. Crystal data: (10) orthorhombic, space group *P*2₁2₁2₁, *a* = 6.607(2) Å, *b* = 10.459(2) Å, *c* = 15.411(3) Å, *Z* = 4, *R*₁ = 0.0920 for 138 parameters and 1787 observed reflections; (11) monoclinic, space group *P*2₁/*a*, *a* = 7.1237(7) Å, *b* = 20.257(2) Å, *c* = 8.1669(8) Å, β = 96.73(1)°, *Z* = 4, *R*₁ = 0.0367 for 184 parameters and 3211 observed reflections; (14a) orthorhombic, space group *P*2₁2₁2₁, *a* = 8.6105(8) Å, *b* = 9.5644(8) Å, *c* = 29.271(3) Å, *Z* = 4, *R*₁ = 0.0423 for 300 parameters and 4497 observed reflections; (15b) orthorhombic, space group *P*2₁2₁2₁, *a* = 6.7400(9) Å, *b* = 12.526(3) Å, *c* = 24.254(4) Å, *Z* = 4, *R*₁ = 0.0454 for 246 parameters and 3387 observed reflections.

1. Introduction

There is currently a resurgence of interest in acyclic (diene)Fe(CO)₃ complexes as organic intermediates, perhaps best exemplified by the independent approaches of three groups to leukotriene synthesis.¹⁻³ For synthetic reasons, these studies have focused entirely on complexes containing electron withdrawing aldehyde and ester substituents. Despite the well recognized regio-directing power of electron donor substituents such as methoxy in cyclic [(dienyl)Fe(CO)₃]X complexes,⁴ the chemistry of neutral or cationic acyclic complexes containing electron donor substituents remains relatively unexplored. Work on neutral complexes has been concerned with attack by carbon-centered nucleophiles on (2-methoxybutadiene)-Fe(CO)₃ and both (*E*)- and (*Z*)-(1-methoxybutadiene)-Fe(CO)₃; addition occurs mainly at the internal carbon to give [(η¹,η²-but-3-en-1-yl)Fe(CO)₃]⁻ anions which on protonation or alkylation in the presence of CO give either cyclopentanones and γ,δ-unsaturated aldehydes or ketones.⁵⁻⁹

Acyclic dienyl salts containing electron donor substituents are rare,¹⁰ and few potential precursors of structure 1 containing reduceable α-carbonyl substituents have been reported.¹¹

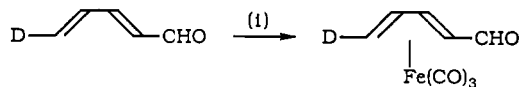


(1)

We wish to report here the preparation of such precursors, together with methods for their resolution and assignment of absolute configuration.

2. Synthesis and Resolution

Dienes 2, 3, 5, and 6 were prepared by acylation of sodium glutacetaldehyde or the ring opening of (2,4-dinitrophenyl)pyridiniumchloride with the appropriate secondary



- (2) D = OCOMe
 (3) D = OCOPh
 (4) D = OMe
 (5) D = NMe₂
 (6) D = NMePh
 (7) D = (S)-N(Me)CHMePh

- (8) D = OCOMe
 (9) D = OCOPh
 (10) D = OMe
 (11) D = NMe₂
 (12) D = NMePh
 (13a,b) D = (S)-N(Me)CHMePh

(i) ultrasound, Fe₂(CO)₉, toluene
2-6 hours

amine.¹² The crystallized products exhibit NMR spectra consistent with the presence of the (2*E*,4*E*) isomer only.

(10) During the course of this work, the preparation of [(1-methyl-4-methoxypentadienyl)Fe(CO)₃]PF₆ was reported: Donaldson, W. A.; Jin, M. *J. Bull. Soc. Chim. Belg.* 1993, 102, 297.

(11) We are aware only of the complexes (D = CH₃CO, R = CH₃, Ph, H) prepared by ring opening of (2-pyrone)Fe(CO)₃: DuPuy, C. H.; Parton, R. L.; Jones, T. *J. Am. Chem. Soc.* 1977, 99, 4070. Friedel-Crafts acetylation of (1-methoxy- and (2-methoxybutadiene)Fe(CO)₃ is not a viable route: Graf, R. E.; Lillya, C. P. *J. Organomet. Chem.* 1976, 122, 377.

(12) Becher, J. *Synthesis* 1980, 589.

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(2) Franck-Neumann, M.; Colson, P. *J. Synlett* 1991, 891.
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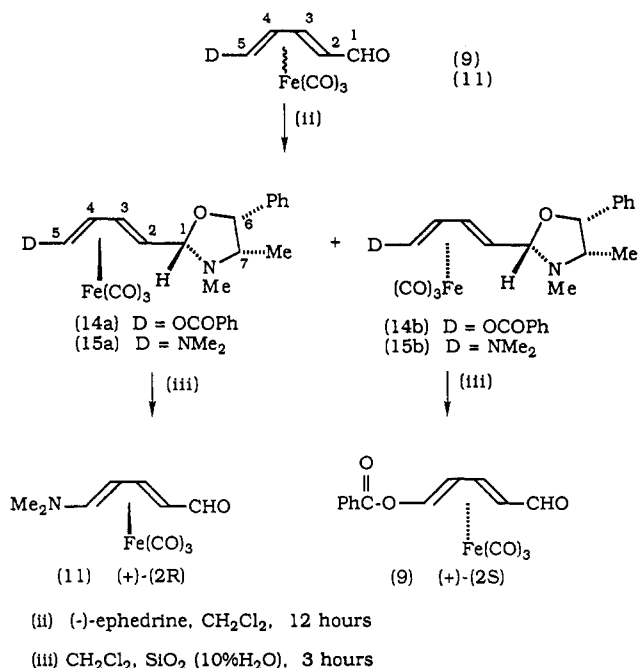
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The somewhat less stable dienes **4** and **7** were prepared respectively by alkylation of sodium glutacetaldehyde with methyl *p*-toluenesulfonate in dimethylformamide¹³ and ring opening of (2,4-dinitrophenyl)pyridinium chloride with (-)-(*S*)-*N*-methyl-*N*-(α -methylbenzyl)amine and were reacted directly with Fe₂(CO)₉. NMR spectra of **4** before complexation indicate a 9:1 mixture of (*2E,4E*) and (*2Z,4E*) isomers (see Experimental Section), though only the (*2E,4E*) compound **10** is isolated after complexation. Complexes **8**–**13** are isolated after chromatography as red or orange crystalline solids.

Resolution of **9** and **11** has been effected through the single pair of diastereoisomeric oxazolidines **14a,b** and **15a,b** formed on reaction with (-)-(*1R,2S*)-ephedrine.¹⁴



These diastereoisomers may easily be differentiated in the NMR spectrum by the pairs of doublet resonances assignable to H(1). Single fractional crystallizations provide excellent yields (80–90%) of the pure diastereoisomers **14a** and **15b** from which the homochiral aldehydes **9** and **11** may be regenerated by mild hydrolysis. The absence of racemization during hydrolysis was confirmed by chiral shift reagent studies.¹⁵ Complexes **14b** and **15a** may be recovered in 72 and 56% ee, respectively, from the residues.

Attempts at the resolution of **10** through oxazolidine or semioxamazone¹⁶ formation failed. Success was achieved through adaption of a method used for the resolution of chiral (benzaldehyde)Cr(CO)₃ derivatives.¹⁷ Reaction with (+)-(*S*)-valinol yields a pair of imine diastereoisomers

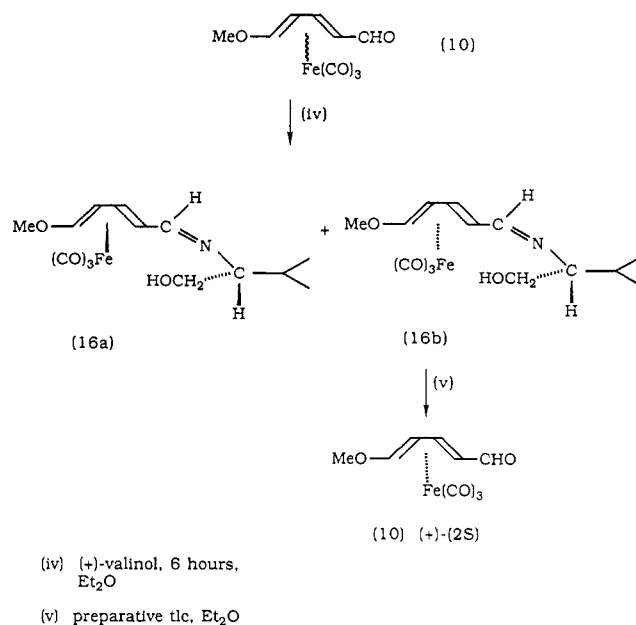
(13) Compound **10** has been reported as the major product of ozonolysis of 1,3-cyclopentadiene: Griesbaum, K.; Jung, I. C.; Mertens, H. *J. Org. Chem.* 1990, 55, 6024. The analogous trimethylsiloxy compound has been prepared but is unstable above -10 °C: Lewis, N.; McKen, P. W.; Taylor, R. J. K. *Synlett.* 1991, 898.

(14) Monpert, A.; Martelli, J.; Grée, R.; Carrié, R. *Tetrahedron Lett.* 1981, 22, 1961.

(15) The shift reagent used in all NMR studies was tris[3-(heptafluoropropyl)hydroxymethylene]-(+)-camphorato]Eu^{III}.

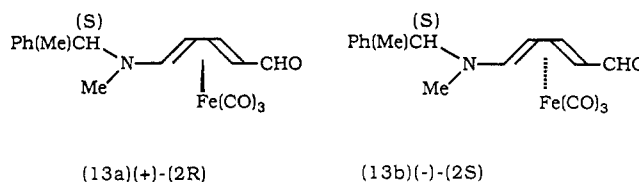
(16) Franck-Neumann, M.; Martina, D.; Heitz, M. P. *J. Organomet. Chem.* 1986, 301, 61.

(17) (a) Davies, S. G.; Goodfellow, C. L. *J. Chem. Soc., Perkin Trans. 1* 1989, 192. (b) Davies, S. G.; Goodfellow, C. L. *J. Chem. Soc., Perkin Trans. 1* 1990, 393. (c) Bromley, L. A.; Davies, S. G.; Goodfellow, C. L. *Tetrahedron: Asymmetry* 1991, 2, 139.



(**16a,b**); imine rather than oxazolidine formation is indicated by the pair of H(1) doublets at 7.24 and 7.82 ppm, which can be used as a measure of optical purity. Preparative TLC results in preferential hydrolysis of **16**, eluting first the aldehyde (*2S*)-**10** of 75% ee followed by optically pure **16**. A single recrystallization of enriched **10** gives optically pure material. The opposite (*2R*)-**10** enantiomer may be generated by mild hydrolysis of **16a**.

The planar chirality of the dialkylamino substituted derivatives may also be resolved by chromatographic separation of the 1:1 diastereoisomer mixture **13a,b** formed on complexation of the homochiral diene **7**. Attempts to extend this methodology to alkoxy and acyloxy substituted complexes have not been successful.



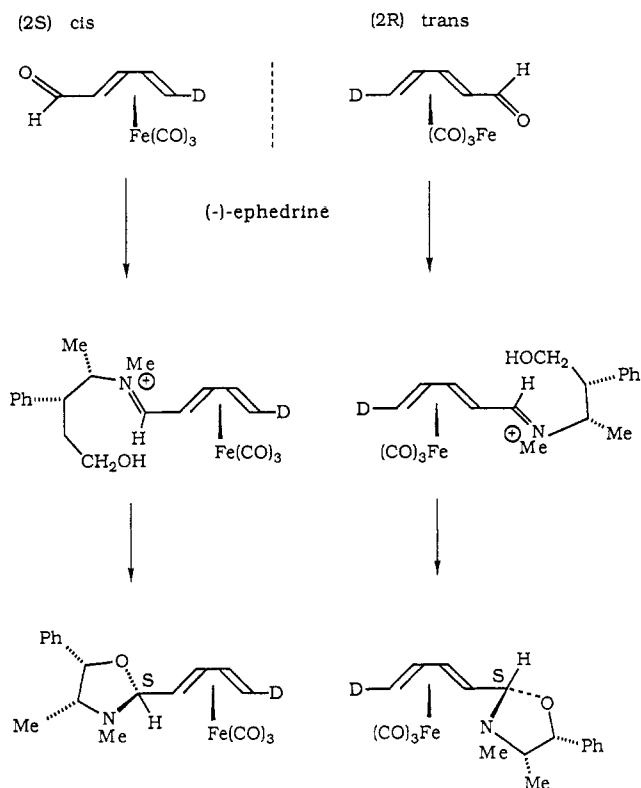
3. Structure and Absolute Configuration

NMR spectra are in agreement with the proposed structures; in particular, the downfield shift of the H(5)/C(5) resonances attached to the donor substituent may be noted.

Absolute configurations have been established through single crystal structure determinations of the oxazolidine diastereoisomers **14a** and **15b** and the homochiral methoxy complex **10**. A structure determination of racemic **11** has also been performed. Complexes **14a** and **15b** have opposite planar chirality, thus giving (*2S*)-**9** and (*2R*)-**11** on regeneration of aldehyde. The configuration of the new chiral C(1) center is, however, (*S*) in both cases, as is the (*6R,7S*) configuration of the moiety derived from (-)-ephedrine.¹⁸ Other organic and organometallic oxazolidines derived from (-)-ephedrine also show (*S*) stereo-

(18) For simplicity, the numbering scheme of the diene has been retained in complexes **14** and **15**; using the conventional numbering for the oxazolidine ring, the configuration is (1*S*,3*R*,4*S*).

chemistry at this new center.^{14,19,20} The results thus imply a reaction that is driven by a thermodynamic preference for this oxazolidine ring stereochemistry. Assuming that the reaction proceeds via an iminium ion intermediate,²¹ the observed product stereochemistry requires reaction of the (2*R*) isomer in the trans conformation but reaction of the (2*S*) isomer in the cis conformation since intramolecular attack to generate the oxazolidine will occur on the face opposite the iron moiety. The solid state structure of 11 indeed reveals a trans configuration. While it has not been possible to grow suitable crystals of 9, the methoxy complex 10 does exhibit a cis configuration. In solution, both conformers may be populated; NMR studies of (sorbalddehyde)Fe(CO)₃ indicate an approximately equal population of cis and trans conformers.^{22,23}



Circular dichroism spectra have also been determined as an aid to assignment of future absolute configurations in this new series. Previous work²⁴ has shown that (diene)-Fe(CO)₃ complexes containing carbonyl chromophores on the (2*S*) carbon exhibit a strong negative band at the longest wavelength. CD spectra of the complexes prepared in this work (Figure 1) support this observation. Spectra of the separated diastereoisomer pair 13*a,b* are essentially mirror images and that of 13*a* is essentially superimposable on that of 11, indicating that the chiral CH(Me)Ph auxiliary has little effect on these long wavelength bands. The reversed signs of the long wavelength bands for 9 and 10 relative to 11 are consistent with the inverted planar

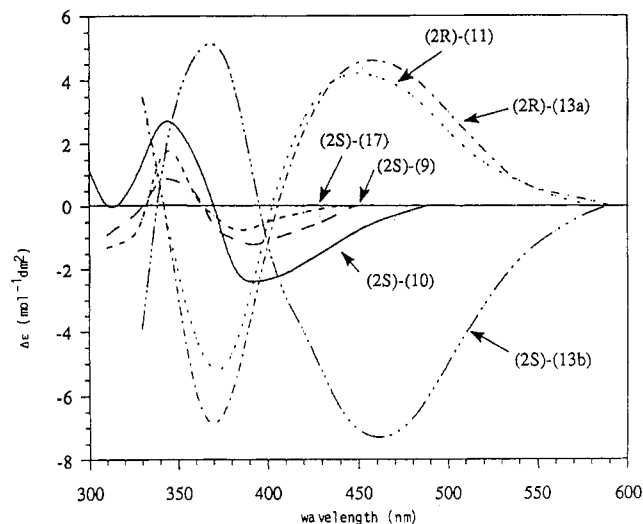
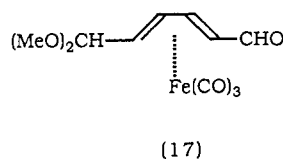


Figure 1. Circular dichroism spectra: CH₃CN solution; data for 17 in MeOH taken from ref 23.

chirality established from the crystallographic studies. There is an increase in intensity and a shift to longer wavelength in the order OCOPh < OMe < NMe₂, consistent with the increase in electron donor character of the heterosubstituent.²⁵ Shown for comparison is the spectrum of (2*S*)-17, a complex in which the saturated 5-substituent has little effect on the circular dichroism spectrum.



Other structural features (Figure 2, Table 1) are also consistent with an electron donation which increases in the order OCOPh < OMe < NMe₂. In all cases, the plane of the heterosubstituent deviates little from coplanarity with the diene. The deviation is greatest for the most sterically demanding NMe₂ substituent, and the tilting is such that the syn carbons [C(7) in 11 and C(10) in 15*b*] are moved closer to the iron. The aldehyde groups in 10 and 11 are also essentially coplanar with the diene; the oxygen is tilted toward the iron in the cis conformation of 10 but away from the iron in the trans conformation of 11. For both 14*a* and 10, a slight shortening of the C(terminal)-O bond relative to values typical of saturated benzoate esters²⁶ and ethers²⁷ is observed, though there is no significant difference in the C(terminal)-O-C angles. More dramatic changes are seen in 11 and 15*b*, which are essentially isostructural in terms of the geometries of the diene-Fe and NMe₂ moieties. The C(terminal)-N bond is severely shortened (1.35 Å) relative to the N-Me bonds (1.46 Å), and bond angles show that the nitrogen ap-

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(24) Djedani, F.; Grée, D.; Martelli, J.; Grée, R.; Leroy, L.; Bolard, J.; Toupet, L. *Tetrahedron Lett.* 1989, 30, 3781.

(25) This ordering is also found for the activation of benzene toward electrophilic substitution: Sykes, P. *A Guidebook to Mechanism in Organic Chemistry*, 6th ed.; Longman Scientific: Harlow, U.K., 1986; p 155.

(26) C-OCOPh and C-O-COPh values for saturated benzoate esters are approximately 1.49 Å and 117°. Palmer, A.; Poulin-Dandurand, S.; Brisse, F. *Can. J. Chem.* 1985, 63, 3079.

(27) C-O and C-O-C values for the dimethyl ether are 1.42 Å and 111°. Tamagawa, M.; Takemura, M.; Konaka, S.; Kimura, M. *J. Mol. Struct.* 1984, 125, 131. Values similar to those of 10 have been observed in organic vinyl ethers: Barker, A. J.; Begley, M. J.; Birch, A. M.; Pattenden, G. *J. Chem. Soc., Perkin Trans 1* 1983, 1919.

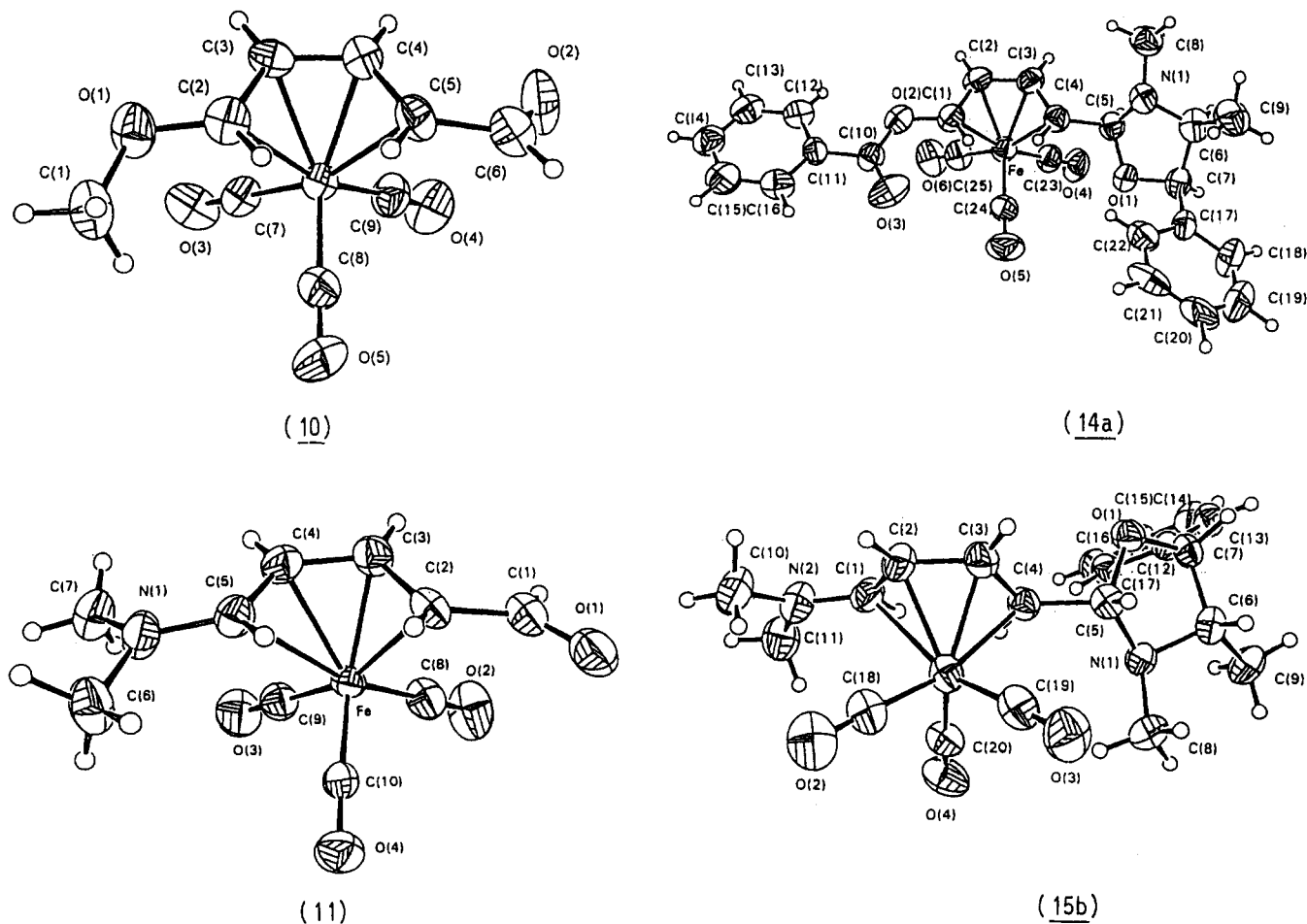


Figure 2. Molecular structures of 10, 11, 14a, and 15b.

Table 1. Important Bond Lengths (Å) and Angles (deg)

	11	(2 <i>R</i>)-15b	(2 <i>S</i>)-14a	(2 <i>S</i>)-10
Fe-CO(av)	1.781(3)	1.771(4)	1.791(4)	1.789(10)
Fe-C(terminal) ^a	2.459(2)	2.465(4)	2.110(4)	2.160(10)
Fe-C(terminal) ^b	2.111(2)	2.123(3)	2.116(3)	2.124(10)
Fe-C(internal) ^c	2.126(3)	2.106(4)	2.060(4)	2.081(9)
Fe-C(internal) ^d	2.011(3)	2.033(4)	2.042(4)	2.033(10)
C _{basal} -Fe-CO _{basal}	89.8(1)	88.2(2)	91.0(2)	90.6(5)
C _{basal} -Fe-CO _{axial} (av)	102.8(1)	104.9(2)	101.4(2)	101.8(5)
P1-P2 ^e	22.8	22.0	3.5	10.3 ^f
P1-P3	20.3			16.7

11		(2 <i>R</i>)-15b		(2 <i>S</i>)-14a		(2 <i>S</i>)-10	
C5-N1	1.342(3)	C1-N2	1.336(4)	C1-O2	1.405(5)	C2-O1	1.378(12)
C6/7-N1	1.448(4)	C10/11-N2	1.462(5)	C10-O2	1.342(5)	C1-O1	1.414(13)
C5-N1-C6	118.8(2)	C1-N2-C10	122.0(4)	C10-O3	1.181(5)	C1-O1-C2	113.2(9)
C5-N1-C7	122.3(3)	C1-N2-C11	118.9(4)	C10-C11	1.487(5)		
C6-N1-C7	116.793	C10-N2-C11	117.5(4)	C1-O2-C10	117.0(3)		
				C11-C10-O2	112.2(3)		

^a α to donor substituent. ^b δ to donor substituent. ^c β to donor substituent. ^d γ to donor substituent. ^e P1 = plane of diene, P2 = plane of donor substituent, P3 = plane of CHO. ^f C1-O2-C2-C3 dihedral angle.

proaches sp² hybridization (\angle C-N-C(av) = 118°).²⁸ Indeed, restricted C-NMe₂ rotation is evident in the resolution of the NMe₂ ¹H resonance into two at low temperature (ΔG_c^\ddagger = 44.8 kJ mol⁻¹).²⁹ The spectrum of 12 is temperature independent, indicating that only a single conformer is present.

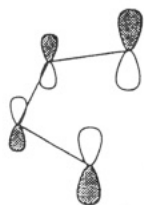
(28) The N-C and C-N-C values for NMe₂ are 1.46 Å and 111°: Beagley, B.; Medwid, A. R. *J. Mol. Struct.* 1977, 38, 229. The crystal structure of the *N*-morpholinyl analogue of 5 has been determined and shows a C(diene)-N bond length of 1.34 Å; Kulpe, S.; Schulz, B. *Krist. Tech.* 1976, 11, 707.

Molecular orbital³⁰ analyses indicate that donor and acceptor substituents differ considerably in their effect on the important butadiene molecular orbitals 18 and 19.³¹ Electron acceptor substituents such as CN decrease the energy of 19 while little affecting 18, thus increasing the π -acceptor capacity of the diene; electron donor substituents (OH, NH₂) increase the energy of both 18 and 19, thus making the diene a better donor but poorer π -acceptor. This effect is more marked for NH₂ than OH. Structurally, this effect seems most manifest in the marked elongation of the Fe-C(terminal) and Fe-C(internal) bonds adjacent

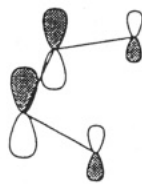
Table 2. Crystallographic Data^a

	10	11	14a	15b
empirical formula	C ₉ H ₈ FeO ₅	C ₁₀ H ₁₁ FeNO ₄	C ₂₅ H ₂₃ FeNO ₆	C ₂₀ H ₂₄ FeN ₂ O ₄
fw	252.00	265.05	489.29	412.26
temp (K)	293(2)	293(2)	293(2)	293(2)
wavelength (Å)	0.710 69	0.710 69	0.710 69	0.710 69
cryst syst	orthorhombic	monoclinic	orthorhombic	orthorhombic
space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /a	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
unit cell dimens				
<i>a</i> (Å)	6.607(2)	7.1237(7)	8.6105(8)	6.7400(9)
<i>b</i> (Å)	10.459(2)	20.257(2)	9.5644(8)	12.526(3)
<i>c</i> (Å)	15.411(3)	8.1669(8)	29.271(3)	24.254(4)
α (deg)	90	90	90	90
β (deg)	90	96.730(10)	90	90
γ (deg)	90	90	90	90
volume (Å ³)	1064.9(5)	1170.4(2)	2410.6(4)	2047.6(7)
Z	4	4	4	4
density (calcd) (Mg/m ³)	1.572	1.504	1.348	1.337
abs coeff (mm ⁻¹)	1.413	1.286	0.665	0.763
F(000)	512	544	1016	864
cryst size (mm)	0.50 × 0.06 × 0.05	0.24 × 0.10 × 0.14	0.55 × 0.42 × 0.18	0.55 × 0.27 × 0.30
θ range for data collection (deg)	2.35–29.95	2.01–31.96	2.24–31.96	2.34–29.97
index ranges	0 ≤ <i>h</i> ≤ 9, 0 ≤ <i>k</i> ≤ 14, 0 ≤ <i>l</i> ≤ 20	0 ≤ <i>h</i> ≤ 8, 0 ≤ <i>k</i> ≤ 22, -9 ≤ <i>l</i> ≤ 9	-4 ≤ <i>h</i> ≤ 12, -2 ≤ <i>k</i> ≤ 14, 0 ≤ <i>l</i> ≤ 35	0 ≤ <i>h</i> ≤ 9, 0 ≤ <i>k</i> ≤ 17, 0 ≤ <i>l</i> ≤ 34
no. of rflns colld	1801	3454	4579	3447
no. of ind rflns	1787 [<i>R</i> (int) = 0.0091]	3211 [<i>R</i> (int) = 0.0158]	4447 [<i>R</i> (int) = 0.0165]	3387 [<i>R</i> (int) = 0.0125]
refinement method	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²	full-matrix least squares on <i>F</i> ²
no. of data/restraints/params	1787/0/138	3211/0/184	4447/0/300	3387/0/246
goodness-of-fit on <i>F</i> ²	0.865	0.937	0.793	1.018
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0920, <i>R</i> _{w2} = 0.2238	<i>R</i> ₁ = 0.0367, <i>R</i> _{w2} = 0.0923	<i>R</i> ₁ = 0.0423, <i>R</i> _{w2} = 0.1165	<i>R</i> ₁ = 0.0454, <i>R</i> _{w2} = 0.1195
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1395, <i>R</i> _{w2} = 0.2650	<i>R</i> ₁ = 0.0903, <i>R</i> _{w2} = 0.1044	<i>R</i> ₁ = 0.1011, <i>R</i> _{w2} = 0.1402	<i>R</i> ₁ = 0.0643, <i>R</i> _{w2} = 0.1286
absolute structure param	0.03(10)		-0.03(2)	-0.02(2)
largest diff peak and hole (e/Å ³)	+1.080 and -2.740	+0.493 and -0.359	+0.370 and -0.236	+0.596 and -0.251

^a *R*₁ = [Σ|*F*_o - *F*_c|]/Σ|*F*_o| (based on *F*'s); *R*_{w2} = [(Σ*w*(*F*_o - *F*_c)²)/Σ*w*(*F*_o)²]^{1/2} (based on *F*'s). *w* = *q*/[(σ*F*_o)² + (*a***P*)² + *b***P* + *d* + *e** sin θ]. Goodness of fit = [Σ*w*(*F*_o² - *F*_c²)²/(*N*_{observ} - *N*_{params})]^{1/2}.

π₂

(18)

π₃

(19)

to the NMe₂ substituent in 11 and 15b. This elongation is present, though less marked, in 10 and appears absent in 14a.

Other data indicate that the dialkylamino derivatives are particularly electron rich. Thus the C–O stretching modes for complexes 11–13 are shifted to lower wavenumbers relative to values for complexes 8–10 and while the ¹³CO subspectra of 8–10 are resolved into axial and basal resonances at -60 °C, the spectrum of 11 retains a single ¹³CO resonance down to -100 °C. It is known that the barriers to diene–Fe rotation are sensitive to the diene substituent, decreasing with the increasing electron donor nature of the diene substituent.³²

(29) Calculated using the equation Δ*G*_c[‡] = (1.914 × 10⁻²)*T*_c[9.972 + log *T*_c/Δ*ν*]. Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: 1982; p 96. For 1b, *T*_c = 218 K and Δ*ν* = 36.9 Hz. The spectrum of the free ligand (5) exhibits a similar temperature dependence from which a slightly higher barrier of Δ*G*_c[‡] = 54.5 kJ mol⁻¹ may be calculated (*T*_c = 268 K, Δ*ν* = 58.8 Hz).

(30) Rao, V. P.; Chandrasekhar, J.; Ramamurthy, V. *J. Chem. Soc., Perkin Trans. 2* 1988, 647.

Preliminary results indicate that, in the form of their Fe(CO)₂PPh₃ derivatives, complexes 9 and 10 may be converted into 1-benzoyloxy- and 1-methoxypentadienyl salts. Full studies of the regio- and stereoselectivity of the reactions of these salts with nucleophiles will be reported in due course.

Experimental Section

Dienes 2, 3, 5, and 6,¹² (-)-(*S*)-*N*-methyl-*N*-(α-methylbenzyl)-amine,³³ sodium glutacetaldehyde, and (2,4-dinitrophenyl)pyridinium chloride¹² were prepared by literature methods. All reactions involving metal complexes were performed using dry, degassed solvents under a nitrogen atmosphere. Infrared and NMR spectra were recorded on Perkin-Elmer 257 and JEOL GSX 270 spectrometers, respectively. Preparative thin layer chromatography was performed on a Harrison Research Model 7924 chromatotron using 2-mm silica gel plates (Type PF60₂₅₄). Quoted NMR chemical shifts are relative to TMS (¹H and ¹³C).

(a) **Preparation of 4.** Methyl *p*-toluenesulfonate (4.2 g, 22 mmol) in dimethylformamide (5 mL) was added to a stirred mixture of sodium glutacetaldehyde (3.0 g, 19 mmol) in dimethylformamide (4 mL). The mixture was heated at 75 °C for 45 min. Water (100 mL) was added to the cooled mixture, which was extracted with diethyl ether (4 × 100 mL) and dried over MgSO₄. Removal of solvent gave 4 (1.79 g, 79%) as a light yellow liquid with a 1:9 (2*Z*,4*E*):(2*E*,4*E*) ratio. ¹H NMR of (2*E*,4*E*) isomer (CDCl₃): δ 9.60 (H(1), d, *J*₁₂ = 8.1 Hz), 7.19–7.31 (H(3), 5, m), 6.23 (H(2), dd, *J*₂₃ = 15.1 Hz), 5.94 (H(4), t), 3.91 (Me, s). Resonances assignable to the (2*Z*,4*E*) isomer can be seen at 9.66

(31) For a molecular orbital analysis of (butadiene)Fe(CO)₃, see: Albright, T. A.; Hoffmann, R. *Chem. Ber.* 1978, 111, 1591.

(32) See ref 22 and references therein.

(33) Brunner, H.; Scheck, T. *Chem. Ber.* 1992, 125, 692.

Table 3. Atomic Coordinates ($\times 10^4$) for 10

	x	y	z
Fe(1)	8692(2)	5186(1)	3788(1)
O(1)	7818(13)	2474(7)	3023(5)
O(2)	7276(16)	8443(8)	3252(7)
O(3)	12218(15)	3574(10)	4000(6)
O(4)	6505(19)	4512(9)	5373(5)
O(5)	11033(18)	7418(9)	4346(6)
C(1)	6923(25)	1718(10)	3680(7)
C(2)	7180(18)	3728(9)	3036(6)
C(3)	8198(16)	4595(9)	2516(5)
C(4)	7855(22)	5904(9)	2616(6)
C(5)	6307(19)	6266(8)	3225(6)
C(6)	6173(24)	7634(11)	3472(8)
C(7)	10839(14)	4231(10)	3911(6)
C(8)	7314(18)	4752(9)	4772(6)
C(9)	10112(21)	6575(11)	4105(8)

Table 4. Atomic Coordinates ($\times 10^4$) for 11

	x	y	z
Fe(1)	6123(1)	3533(1)	3303(1)
O(1)	7604(3)	4778(1)	6875(3)
O(2)	8316(4)	2835(1)	6015(3)
O(3)	5667(4)	2300(1)	1464(3)
O(4)	2380(3)	3664(1)	4415(3)
N(1)	3735(3)	4068(1)	-370(3)
C(1)	8112(4)	4512(1)	5673(4)
C(2)	7061(4)	4487(1)	4044(3)
C(3)	7968(4)	4221(1)	2720(3)
C(4)	6851(4)	4067(2)	1228(3)
C(5)	4926(4)	4238(1)	959(3)
C(6)	1743(5)	4229(2)	-403(5)
C(7)	4221(7)	3584(2)	-1545(4)
C(8)	7495(5)	3110(1)	4951(4)
C(9)	5846(4)	2785(1)	2185(4)
C(10)	3817(4)	3614(1)	3937(3)

(H(1), d, $J_{12} = 8.3$ Hz), 7.65 (H(5), dd), 6.51 (H(3), d), 5.51 (H(4), dd), and 3.90 (Me, s).

(b) Preparation of 7. (S)-(-)-N-Methyl-N-(α -methylbenzyl)-amine (3.0 g, 22 mmol) was added to a stirred solution of (2,4-dinitrophenyl)pyridinium chloride (3.2 g, 11 mmol) in ethanol (30 mL). After heating at 75 °C for 1.5 h, the mixture was poured into water (100 mL), filtered through Celite, and stirred for a further 1.5 h after addition of 5 M NaOH (30 mL). The mixture was extracted with CHCl₃ (3 \times 50 mL) and dried over Na₂SO₄. Preparative TLC of the residue (1:4 ethyl acetate/40–60 petroleum ether) separated unreacted amine from the product to give 7 (1.5 g, 33%) as a yellow oil. ¹H NMR (CDCl₃): δ 9.27 (H(1), d, $J_{12} = 8.3$), 6.9–7.5 (H(3), 5, Ph, m), 5.87 (H(2), dd, $J_{23} = 14.4$), 5.34 (H(4), t), 4.50 (CH, q), 2.66 (NMe, s), 1.58 (Me, d). Minor resonances due to a trace of the (2Z,4E) isomer may also be identified.

(c) Preparation of 10. 5-Methoxy-2,4-pentadienal (1.0 g, 8.9 mmol) and Fe₂(CO)₉ (10 g, 27 mmol) were sonolyzed in toluene (25 mL) until infrared sampling indicated completion. Diethyl ether (30 mL) was added and the solvent was evaporated after filtration through Celite. The product was purified by preparative TLC (1:4 ethyl acetate/40–60 petroleum ether) to give 10 (1.32 g, 57%). An analytical sample was obtained by sublimation (56 °C/0.01 mmHg). Mp: 58–59 °C. Anal. Calcd (found): C, 42.9 (43.1); H, 3.71 (3.14). Infrared (hexane): 2059, 2002, 1987 cm⁻¹. ¹H NMR (C₆D₆): δ 8.90 (H(1), d), 0.31 (H(2), dd), 4.90 (H(3), dd), 4.60 (H(4), t), 2.87 (H(5), d), 2.82 (Me, s). ¹³C NMR (CD₂Cl₂, -60 °C): δ 197.2 (C(1)), 61.5 (C(2)), 77.8, 78.9, 104.1 (C(3–5)), 52.6 (Me), 207.3, 209.5 (CO_{basal}), 215.4 (CO_{axial}).

Other complexes were prepared in the same way.

8: purified by column chromatography (grade IV alumina, 1:4 ethyl acetate/40–60 petroleum ether) and recrystallization from 60–80 petroleum ether (65% yield). Mp: 84–85 °C. Anal. Calcd (found): C, 42.9 (42.8); H, 2.86 (2.72). Infrared (hexane): 2063, 2011, 1993 cm⁻¹. ¹H NMR (C₆D₆): δ 8.99 (H(1), d), 0.33 (H(2), dd), 5.01 (H(3), dd), 4.59 (H(4), t), 4.06 (H(5), d), 1.42 (Me, s). ¹³C NMR (CD₂Cl₂, -50 °C): δ 196.1 (C(1)), 52.1 (C(2)), 77.3, 80.0,

Table 5. Atomic Coordinates ($\times 10^4$) for 14a

	x	y	z
Fe(1)	1562(1)	3927(1)	842(1)
N(1)	-349(4)	4242(3)	2253(1)
O(1)	1999(3)	4980(3)	2005(1)
O(2)	1063(3)	1061(3)	373(1)
O(3)	3223(5)	157(4)	659(1)
O(4)	1791(5)	6967(3)	952(1)
O(5)	4581(4)	3131(4)	1222(2)
O(6)	2120(6)	4157(5)	-140(1)
C(1)	828(5)	1833(4)	776(1)
C(2)	-441(5)	2780(5)	755(1)
C(3)	-601(4)	3715(4)	1120(1)
C(4)	484(4)	3633(4)	1485(1)
C(5)	487(5)	4716(4)	1847(1)
C(6)	238(6)	5120(4)	2621(2)
C(7)	1951(5)	5374(4)	2478(1)
C(8)	-2033(5)	4346(5)	2196(2)
C(9)	-8(6)	4479(6)	3090(2)
C(10)	2287(5)	192(4)	364(1)
C(11)	2318(5)	-681(4)	-56(1)
C(12)	1256(5)	-510(5)	-401(1)
C(13)	1293(6)	-1386(6)	-778(2)
C(14)	2372(6)	-2441(5)	-800(2)
C(15)	3417(7)	-2602(5)	-459(2)
C(16)	3412(6)	-1725(5)	-83(2)
C(17)	3166(5)	4587(4)	2734(1)
C(18)	3929(7)	5218(6)	3096(2)
C(19)	5035(9)	4507(11)	3343(2)
C(20)	5377(7)	3213(11)	3238(3)
C(21)	4683(6)	2534(6)	2877(2)
C(22)	3580(6)	3225(5)	2628(2)
C(23)	1667(5)	5787(4)	908(1)
C(24)	3418(5)	3445(5)	1065(2)
C(25)	1921(6)	4078(5)	240(1)

Table 6. Atomic Coordinates ($\times 10^4$) for 15b

	x	y	z
Fe(1)	-3953(1)	-3547(1)	-1998(1)
O(1)	-5830(4)	-1755(2)	-528(1)
O(2)	-5327(7)	-5327(2)	-2744(1)
O(3)	-976(6)	-4543(3)	-1292(1)
O(4)	-2066(6)	-1802(3)	-2609(1)
N(1)	-2740(4)	-1376(2)	-862(1)
N(2)	-7822(6)	-3243(3)	-2912(1)
C(1)	-7163(6)	-3026(3)	-2405(2)
C(2)	-7054(6)	-3739(3)	-1966(2)
C(3)	-6224(6)	-3445(3)	-1449(1)
C(4)	-5154(5)	-2480(2)	-1406(1)
C(5)	-4256(5)	-2202(2)	-856(1)
C(6)	-2810(6)	-981(3)	-291(1)
C(7)	-5037(6)	-896(3)	-200(1)
C(8)	-770(6)	-1759(3)	-1021(2)
C(9)	-1633(7)	36(3)	-201(2)
C(10)	-8208(8)	-4329(4)	-3095(2)
C(11)	-7708(9)	-2408(4)	-3336(2)
C(12)	-5944(5)	155(3)	-360(1)
C(13)	-6391(7)	906(3)	39(2)
C(14)	-7165(8)	1891(3)	-99(2)
C(15)	-7481(7)	2149(3)	-645(2)
C(16)	-7068(7)	1398(3)	-1047(2)
C(17)	-6291(6)	414(3)	-911(1)
C(18)	-3570(7)	-4622(3)	-2455(2)
C(19)	-2168(7)	-4125(3)	-1556(2)
C(20)	-2829(7)	-2483(3)	-2375(2)

86.7 (C(3–5)), 20.7 (Me), 168.8 (CO₂Me), 205.5, 207.6 (CO_{basal}), 212.7 (CO_{axial}).

9: purified in the same way as 8 (62% yield). Mp: 153–155 °C. Anal. C, 52.6 (52.8); H, 2.92 (2.84). Infrared (hexane): 2068, 1998 cm⁻¹. ¹H NMR (C₆D₆): δ 8.90 (H(1), d), 0.35 (H(2), dd), 5.11 (H(3), dd), 4.59 (H(4), t), 4.06 (H(5), d), 6.8–7.2 (Ph, m). ¹³C NMR (CD₂Cl₂, -60 °C): δ 196.2 (C(1)), 52.1 (C(2)), 77.4, 80.3, 85.8 (C(3–5)), 127–133 (Ph), 163.9 (CO₂Ph), 205.4, 207.6 (CO_{basal}), 212.7 (CO_{axial}).

11: Purified by column chromatography (deactivated alumina, diethyl ether) and recrystallized from ethyl acetate/40–60 pe-

troleum ether (72% yield). Mp: 135–136 °C. Anal. Calcd (found): C, 45.3 (45.4); H, 4.15 (4.26); N, 5.28 (5.17). Infrared (hexane): 2021, 1971, 1951 cm^{-1} . ^1H NMR (C_6D_6): δ 9.14 (H(1), d), 0.93 (H(2), dd), 4.98 (H(3), dd), 3.85 (H(4), dd), 3.38 (H(5), dd), 1.72 (Me, s). ^{13}C NMR (CD_2Cl_2 , -60 °C): δ 198.5 (C(1)), 51.8 (C(2)), 66.0, 72.3, 114.2 (C(3–5)), 37.2, 46.0 (NMe₂), 214.5 (CO).

12: purified in the same way as 11 (52% yield). Mp: 130–132 °C. Anal. Calcd (found): C, 55.1 (54.8); H, 3.95 (3.85); N, 4.28 (4.23). Infrared (CH_2Cl_2): 2035, 1963 cm^{-1} . ^1H NMR (C_6D_6): δ 9.11 (H(1), d), 0.77 (H(2), dd), 5.10 (H(3), dd), 4.19 (H(4), dd), 3.68 (H(5), d), 2.23 (Me, s), 6.7–7.1 (Ph, m). ^{13}C NMR (CD_2Cl_2 , -20 °C): δ 196.7 (C(1)), 51.5 (C(2)), 69.1, 97.8 (C(3–5)), 116–130 (Ph), 34.7 (Me), 212.5 (CO).

13: Diastereoisomers 13a and 13b were separated (in order of elution) by preparative TLC (1:4 ethyl acetate/40–60 petroleum ether) (80% yield). 13a: mp 114–115 °C. Anal. Calcd (found): C, 57.5 (57.7); H, 4.79 (4.90); N, 3.94 (3.95). Infrared (hexane): 2027, 1967, 1951 cm^{-1} . ^1H NMR (C_6D_6): δ 9.18 (H(1), d), 1.03 (H(2), dd), 5.07 (H(3), dd), 3.85 (H(4), 5, m), 3.61 (CH, q), 0.98 (Me, d), 1.68 (NMe, s), 6.7–7.1 (Ph, m). $[\alpha]_{\text{D}}$ (CH_3CN , 1×10^{-3}): +1308. 13b: mp 108–110 °C. Anal. C, 57.5 (57.6); H, 4.79 (4.84); N, 3.94 (3.93). Infrared (hexane): 2027, 1967, 1951 cm^{-1} . ^1H NMR (C_6D_6): δ 9.16 (H(1), d), 1.00 (H(2), dd), 5.03 (H(3), dd), 3.83 (H(4), dd), 3.98 (H(5), d), 3.49 (CH, q), 0.95 (Me, d), 1.81 (NMe, s), 6.8–7.1 (Ph, m). $[\alpha]_{\text{D}}$ (CH_3CN , 1×10^{-3}): -1493.

Coupling constants for the above complexes are typically in the range $J_{23} = 8$ –8.5 Hz, $J_{34} = 6$ –8 Hz. For oxygen substituted complexes, $J_{45} = 6$ –6.5 Hz, whereas for nitrogen substituted complexes, $J_{45} = 11$ –13 Hz. J_{12} values increase in the order OCO (2.5 Hz) < OMe (4.1 Hz) < NR₂ (5.2 Hz), perhaps indicating an increasing proportion of trans-aldehyde conformer.

(c) **Resolution of 9.** Complex 9 (0.3 g, 0.9 mmol) and (-)-ephedrine (0.17 g, 1.0 mmol) were stirred in CH_2Cl_2 (7 mL) overnight. Filtration through Celite and evaporation of solvent gave 14a,b (0.43 g, 96%) as an equimolar mixture, indicated by H(1) doublets of equal intensity at 3.40 and 3.78 ppm. Crystallization of the residue from 1:9 ethyl acetate/60–80 petroleum ether (25 mL) gave pure 14a (0.19 g, 86%). Mp: 157–60 °C. Anal. Calcd (found): C, 61.4 (61.2); H, 4.70 (4.60); N, 2.86 (2.77). Infrared (hexane): 2059, 1999, 1983 cm^{-1} . ^1H NMR (CDCl_3): δ 3.40 (H(1), d), 1.06 (H(2), t), 5.50 (H(3), dd), 5.25 (H(4), dd), 4.42 (H(5), d), 4.98 (H(6), d), 2.81 (H(7), m), 0.63 (Me, d), 2.30 (NMe, s), 7.2–8.0 (Ph, m). Coupling constants are $J_{1-2} = 8.3$, $J_{2-3} = 8.3$, $J_{3-4} = 7.2$, $J_{4-5} = 5.7$, $J_{6-7} = 7.7$, $J_{7-\text{Me}} = 6.3$ Hz. $[\alpha]_{\text{D}}$ (CH_3CN , 1×10^{-3}): -240. The recovered residue contained 14a and 14b in a 1:6 ratio.

Homochiral 9 was regenerated by addition of 14a (0.19 g) to a suspension of silica (3.0 g) deactivated with water (0.3 g) in CH_2Cl_2 (10 mL). After infrared sampling indicated completion, the suspension was filtered and the solvent evaporated to give 9 (0.12 g, 89%). $[\alpha]_{\text{D}}$ (CH_3CN , 1×10^{-3}): +96.

(d) **Resolution of 11.** Complex 11 (0.4 g, 1.5 mmol) and (-)-ephedrine (0.24 g, 1.5 mmol) were stirred in CH_2Cl_2 (7 mL) overnight. Filtration through Celite and evaporation of solvent gave 15a,b (0.57 g, 83%) as an equimolar mixture, indicated by H(1) doublets of equal intensity at 3.41 and 3.72 ppm.

Crystallization of the residue from 1:9 ethyl acetate/60–80 petroleum ether (30 mL) gave pure 15b (0.2 g, 80%). Mp: 145–146 °C. Anal. Calcd (found): C, 58.3 (58.0); H, 5.83 (5.77); N, 6.80 (6.62). Infrared (hexane): 2022, 1951, 1945 cm^{-1} . ^1H NMR

(CDCl_3): δ 3.72 (H(1), d), 0.89 (H(2), t), 5.15 (H(3), dd), 4.78 (H(4), dd), 3.68 (H(5), d), 4.95 (H(6), d), 2.78 (H(7), m), 0.65 (Me, d), 2.45 (NMe, s), 2.51 (NMe₂, s), 7.2–7.35 (Ph, m). Coupling constants are similar to those of 14a. $[\alpha]_{\text{D}}$ (CH_3CN , 1×10^{-3}): +566. The recovered residue contained 15a and 15b in a 3.6:1 ratio.

Hydrolysis of 15b (0.2 g) in a manner similar to that of 14a gave homochiral 11 (0.11 g, 83%). $[\alpha]_{\text{D}}$ (CH_3CN , 1×10^{-3}): +1149.

(e) **Resolution of 10.** Complex 10 (0.75 g, 3 mmol) and (+)-valinol (0.32 g, 3.1 mmol) were stirred in diethyl ether (30 mL) until infrared sampling indicated complete reaction. Evaporation of the solvent gave 16a,b as an equimolar mixture, evidenced by the H(1) doublets of equal intensity at 7.24 and 7.82 ppm. Preparative TLC using diethyl ether eluted a yellow band containing 11 (0.45 g, 60%); a second yellow band containing 16a was eluted with 5:1 diethyl ether/methanol (0.4 g, 40%). NMR analysis showed 16a to be homochiral while 10 had an ee of 75%. Recrystallization of enriched 10 from 60–80 petroleum ether gave homochiral 10 (0.2 g). $[\alpha]_{\text{D}}$ (CH_3CN , 1×10^{-3}): +272.

(f) **Crystallographic Data.** Data were collected on an Enraf-Nonius CAD4F diffractometer using Mo $K\alpha$ radiation. The structures of 10, 11, 14a, and 15b were solved by direct methods (SHELX86)³⁴ and refined by full matrix least squares using SHELXL-93.³⁵ Data were corrected for Lorentz and polarization effects but not for absorption. All structures were refined until the maximum deviation/ESD in any parameter was <0.001. Hydrogen atoms were included in calculated positions with common thermal parameters for 10, 14a, and 15b and were all refined for 11. The non-hydrogen atoms were refined anisotropically. The intensity control reflections indicated that only the crystal of 10 decomposed during data collection. The decomposition was isotropic and a correction was applied. The final intensity was 15% of the original. The relatively high *R* factors in this case are undoubtedly due to this decomposition. The absolute structures of 10, 14a, and 15b were determined crystallographically as follows. The Flack absolute structure parameters were all close to 0.0. On inversion and refinement with the wrong absolute configuration, the Flack parameters for 10, 14a, and 15b increased to 0.84(10), 0.79(03), and 0.86(03) and the *R* indices *R*₁ and *R*_{w2} (all data) increased to (0.1412, 0.2711), (0.1077, 0.1462), and (0.0733, 0.1557), respectively. The ORTEP program was used to obtain the drawings.³⁶ Crystal data are contained in Table 2, and atomic coordinates are listed in Tables 3–6.

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Supplementary Material Available: Tables of crystal data, atomic coordinates, bond lengths and angles, and thermal parameters (22 pages). Ordering information is given on any current masthead page.

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