Access to Homochiral Acyclic (diene)$Fe(CO)_3$ Complexes Containing Electron Donor Substituents

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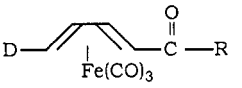
(2,4-pentadienal)$Fe(CO)_3$ complexes containing electron donor 5-substituents (OMe, OCOR, NR_2) have been prepared and resolved via oxazolidine or imine derivatives or through incorporation of a homochiral dialkylamino auxiliary. Absolute configurations have been established by X-ray crystallography. Crystal data: (**10**) orthorhombic, space group $P2_12_12_1$, 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 $P2_1/a$, 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 $P2_12_12_1$, 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 $P2_12_12_1$, 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 sustituents. 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 [(η^1,η^2-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 procursors of structure **1** containing reduceable α-carbonyl substituents have been reported.[11]

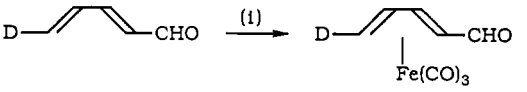


(1)

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 glutaconaldehyde or the ring opening of (2,4-dinitrophenyl)pyridiniumchloride with the appropriate secondary



(2) D = OCOMe
(3) D = OCOPh
(4) D = OMe
(5) D = NMe_2
(6) D = NMePh
(7) D = (S)-N(Me)CHMePh

(8) D = OCOMe
(9) D = OCOPh
(10) D = OMe
(11) D = NMe_2
(12) D = NMePh
(13a,b) D = (S)-N(Me)CHMePh

(i) ultrasound, $Fe_2(CO)_9$, toluene 2-6 hours

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

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(1) Nunn, K.; Mosset, P.; Grée, R.; Saalfrank, R. W. *J. Org. Chem.* **1992,** *57,* 3359.

(2) Franck-Neumann, M.; Colson, P. J. *Synlett* **1991,** 891.

(3) Tao, C.; Donaldson, W. A. *J. Org. Chem.* **1993,** *58,* 2135.

(4) Palotai, I. M.; Stephenson, G. R.; Ross, W. J.; Tupper, D. E. *J. Organomet. Chem.* **1989,** *364,* C11 and references therein.

(5) Semmelhack, M. F.; Hanh, T. M. L. *J. Am. Chem. Soc.* **1984,** *106,* 2715.

(6) Semmelhack, M. F.; Herndon, J. W.; Lu, J. K. *Organometallics* **1983,** *2,* 1885.

(7) Yeh, M. P.; Hwu, C. C. *J. Organomet. Chem.* **1991,** *419,* 341.

(8) Yeh, M. P. *Bull. Inst. Chem., Acad. Sin.* **1990,** 7.

(9) Yeh, M. P.; Chu, C. H.; Sun, M. L.; Kang, K. P. *J. Chin. Chem. Soc.* **1990,** *37,* 547.

(10) During the course of this work, the preparation of [(1-methyl-4-methoxypentadienyl)$Fe(CO)_3$]PF_6 was reported: Donaldson, W. A.; Jin, M. J. *Bull. Soc. Chim. Belg.* **1993,** *102,* 297.

(11) We are aware only of the complexes (D = CH_3CO, R = CH_3, 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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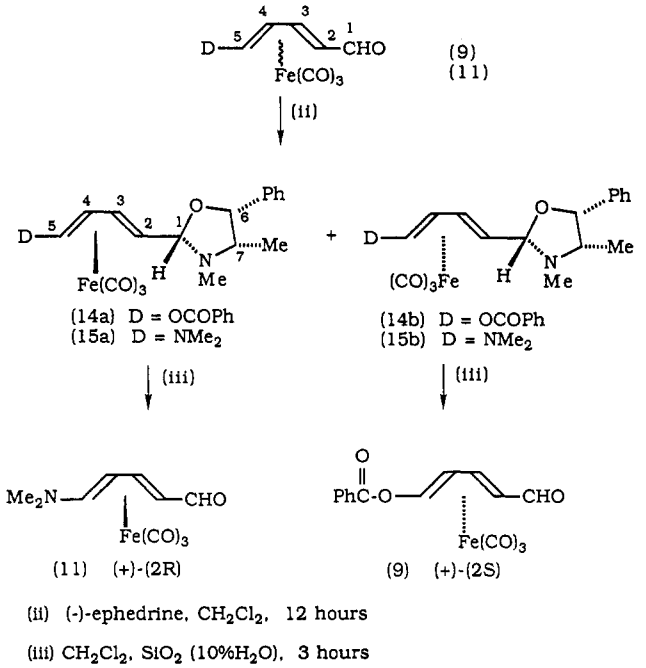
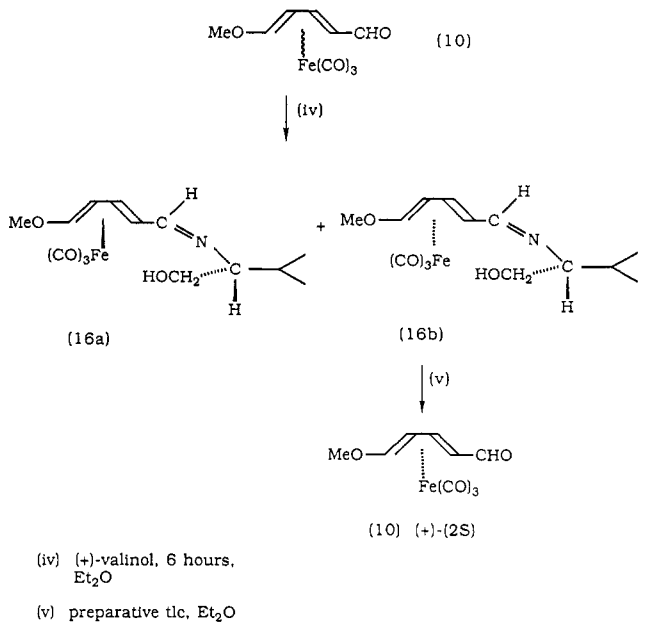
The somewhat less stable dienes **4** and **7** were prepared respectively by alkylation of sodium glutaconaldehyde with methyl *p*-toluenesulfonate in dimethylformamide[13] and ring opening of (2,4-dinitrophenyl)pyridinium chloride with (−)-(*S*)-*N*-methyl-*N*-(α-methylbenzyl)amine and were reacted directly with $Fe_2(CO)_9$. NMR spectra of **4** before complexation indicate a 9:1 mixture of (2*E*,4*E*) and (2*Z*,4*E*) isomers (see Experimental Section), though only the (2*E*,4*E*) 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 (−)-(1*R*,2*S*)-ephedrine.[14]



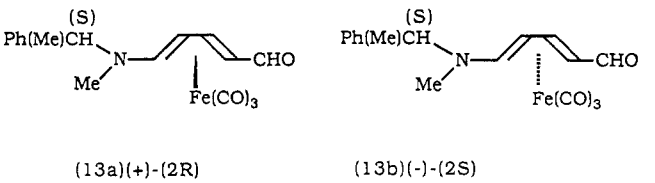
These diastereoisomers may easily be differentiated in the NMR spectrum by the pairs of doublet resonances assignable to H(1). Single fractional crystallizations provide excellent yields (80–90%) of the pure diastereoisomers **14a** and **15b** from which the homochiral aldehydes **9** and **11** may 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 semioxamazone[16] 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



(**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 (2*S*)-**10** of 75% ee followed by optically pure **16**. A single recrystallization of enriched **10** gives optically pure material. The opposite (2*R*)-**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 (2*S*)-**9** and (2*R*)-**11** on regeneration of aldehyde. The configuration of the new chiral C(1) center is, however, (*S*) in both cases, as is the (6*R*,7*S*) configuration of the moiety derived from (−)-ephedrine.[18] Other organic and organometallic oxazolidines derived from (−)-ephedrine also show (*S*) stereo-

(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.

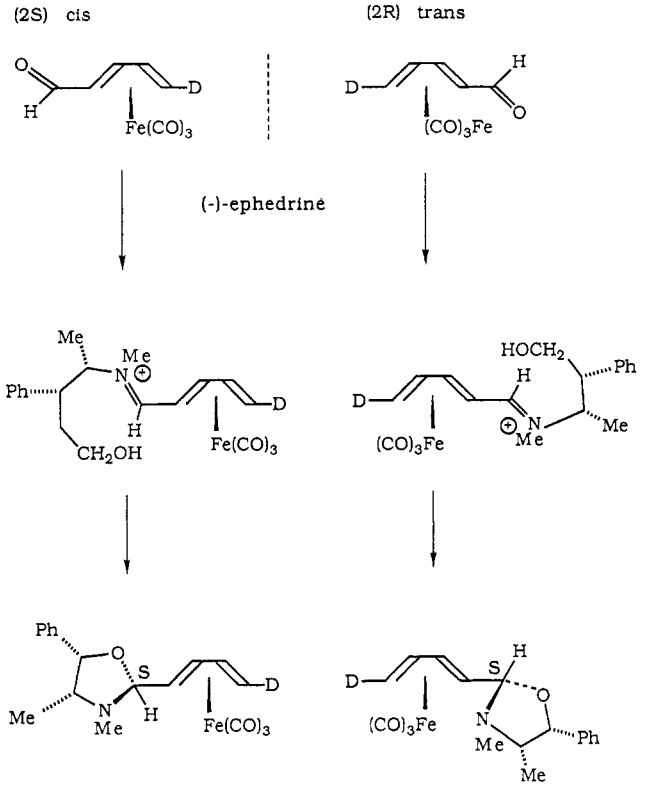
(15) The shift reagent used in all NMR studies was tris[3-((heptafluoropropyl)hydroxymethylene)-(+)-camphorato]Eu^{III}.

(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.

(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 (sorbaldehyde)$Fe(CO)_3$ 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 work[24] 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 **13a,b** are essentially mirror images and that of **13a** 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

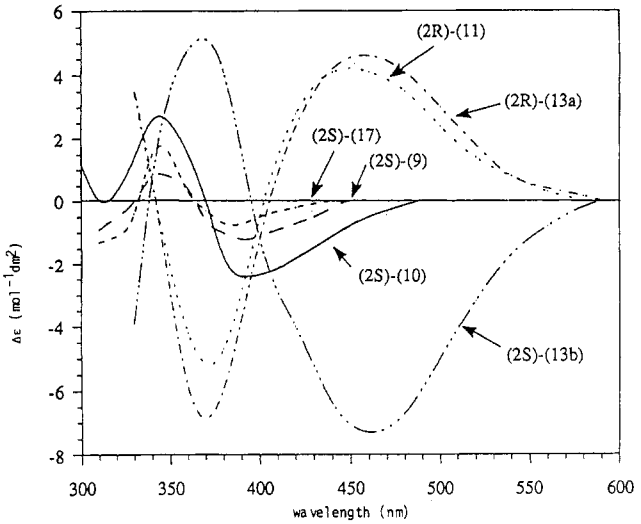
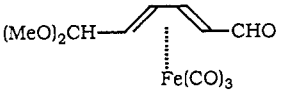


Figure 1. Circular dichrosim spectra: CH_3CN solution; data for **17** in MeOH taken from ref 23.

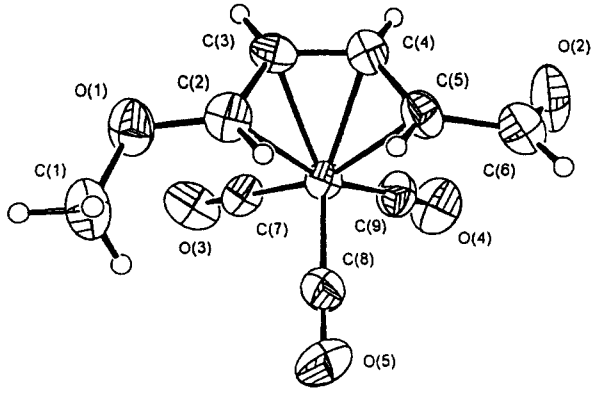
chirality established from the crystallographic studies. There is an increase in intensity and a shift to longer wavelength in the order OCOPh < OMe < NMe_2, consistent with the increase in electron donor character of the heterosubstituent.[25] Shown for comparison is the spectrum of (2*S*)-**17**, a complex in which the saturated 5-substituent has little effect on the circular dichroism spectrum.



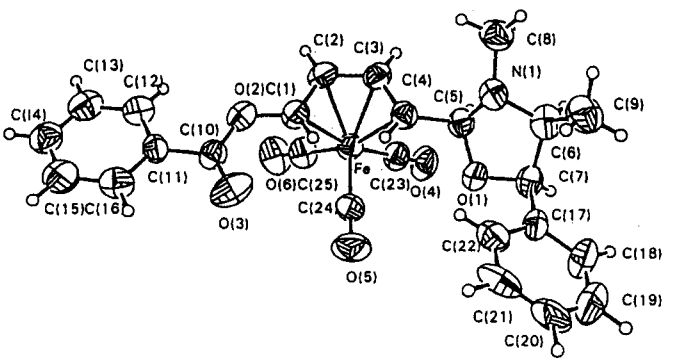
(17)

Other structural features (Figure 2, Table 1) are also consistent with an electron donation which increases in the order OCOPh < OMe < NMe_2. In all cases, the plane of the heterosubstituent deviates little from coplanarity with the diene. The deviation is greatest for the most sterically demanding NMe_2 substituent, and the tilting is such that the syn carbons [C(7) in **11** and C(10) in **15b**] 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 **14a** and **10**, a slight shortening of the C(terminal)–O bond relative to values typical of saturated benzoate esters[26] and ethers[27] is observed, though there is no significant difference in the C(terminal)–O–C angles. More dramatic changes are seen in **11** and **15b**, which are essentially isostructural in terms of the geometries of the diene–Fe and NMe_2 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-

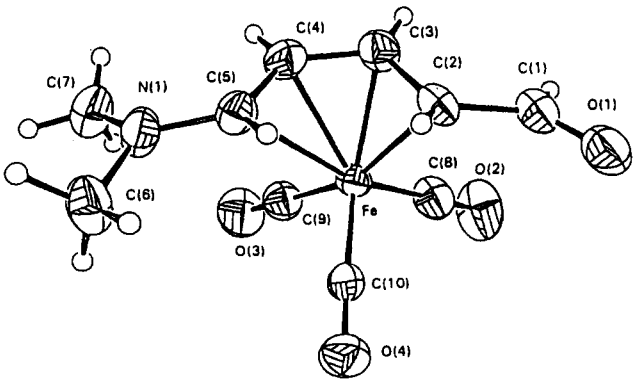
(19) Just, G.; Potvin, P.; Uggowitzer, P.; Bird, P. *J. Org. Chem.* **1983**, *48*, 2923.
(20) Loim, N. M.; Kandratenko, M. A.; Sokolov, V. I.; Turdybekov, K. M.; Struchkov, Y. T. *Metalloorg. Khim.* **1992**, *5*, 1176.
(21) Agami, C.; Rizk, T. *Tetrahedron* **1985**, *41*, 537.
(22) Howell, J. A. S.; Walton, G.; Tirvengadum, M. C.; Squibb, A. D.; McArdle, P.; Cunningham, D.; Goldschmidt, Z.; Gottlieb, H.; Strul, G. *J. Organomet. Chem.* **1991**, *401*, 91.
(23) Brookhart, M.; Harris, D. L. *J. Organomet. Chem.*, **1972**, *42*, 441.
(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.



(10)



(14a)



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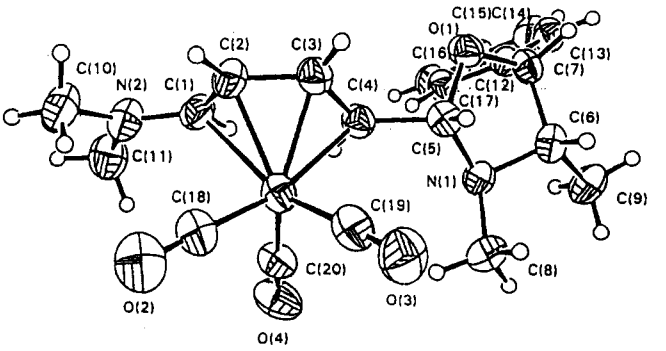


(15b)

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

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

	11	(2*R*)-**15b**	(2*S*)-**14a**	(2*S*)-**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*R*)-**15b**		(2*S*)-**14a**		(2*S*)-**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 sp^2 hybridization (∠C–N–C(av) = 118°).[28] Indeed, restricted C–NMe_2 rotation is evident in the resolution of the NMe_2 ^{1}H resonance into two at low temperature ($\Delta G_c^{\ddagger}$ = 44.8 kJ mol^{-1}).[29] The spectrum of **12** is temperature independent, indicating that only a single conformer is present.

Molecular orbital[30] 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, NH_2) 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 NH_2 than OH. Structurally, this effect seems most manifest in the marked elongation of the Fe–C(terminal) and Fe–C(internal) bonds adjacent

(28) The N–C and C–N–C values for NMe_3 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.

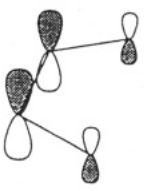
Table 2. Crystallographic Data[a]

	10	11	14a	15b
empirical formula	$C_9H_8FeO_5$	$C_{10}H_{11}FeNO_4$	$C_{25}H_{23}FeNO_6$	$C_{20}H_{24}FeN_2O_4$
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	$P2_12_12_1$	$P2_1/a$	$P2_12_12_1$	$P2_12_12_1$
unit cell dimens				
a (Å)	6.607(2)	7.1237(7)	8.6105(8)	6.7400(9)
b (Å)	10.459(2)	20.257(2)	9.5644(8)	12.526(3)
c (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	$0 \le h \le 9, 0 \le k \le 14, 0 \le l \le 20$	$0 \le h \le 8, 0 \le k \le 22, -9 \le l \le 9$	$-4 \le h \le 12, -2 \le k \le 14, 0 \le l \le 35$	$0 \le h \le 9, 0 \le k \le 17, 0 \le l \le 34$
no. of reflns collcd	1801	3454	4579	3447
no. of ind reflns	1787 [R(int) = 0.0091]	3211 [R(int) = 0.0158]	4447 [R(int) = 0.0165]	3387 [R(int) = 0.0125]
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
no. of data/restraints/params	1787/0/138	3211/0/184	4447/0/300	3387/0/246
goodness-of-fit on F^2	0.865	0.937	0.793	1.018
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0920, R_{w2} = 0.2238	R_1 = 0.0367, R_{w2} = 0.0923	R_1 = 0.0423, R_{w2} = 0.1165	R_1 = 0.0454, R_{w2} = 0.1195
R indices (all data)	R_1 = 0.1395, R_{w2} = 0.2650	R_1 = 0.0903, R_{w2} = 0.1044	R_1 = 0.1011, R_{w2} = 0.1402	R_1 = 0.0643, R_{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] $R_1 = [\sum||F_o| - |F_c||]/\sum|F_o|$ (based on F's); $R_{w2} = [[\sum w(|F_o| - F_c|)^2]/[\sum w(|F_o|)^2]]^{1/2}$ (based on I's). $w = q/[(\sigma F_o)^2 + (a^*P)^2 + b^*P + d + e^* \sin\theta]$. Goodness of fit = $[\sum w(|F_o^2| - F_c^2|)^2/(N_{observus} - N_{params})]^{1/2}$.

π2

(18)



π3

(19)

to the NMe_2 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 ^{13}CO subspectra of **8–10** are resolved into axial and basal resonances at −60 °C, the spectrum of **11** retains a single ^{13}CO 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]

Preliminary results indicate that, in the form of their $Fe(CO)_2PPh_3$ 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 glutaconaldehyde, and (2,4-dinitrophenyl)-pyridinium chloride[12] 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 $PF60_{254}$). Quoted NMR chemical shifts are relative to TMS (^1H and ^{13}C).

(a) Preparation of 4. Methyl *p*-toluenesulfonate (4.2 g, 22 mmol) in dimethylformamide (5 mL) was added to a stirred mixture of sodium glutaconaldehyde (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 $MgSO_4$. 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 ($CDCl_3$): 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

(29) Calculated using the equation $\Delta G_c^{\ddagger} = (1.914 \times 10^{-2})T_c[9.972 + \log T_c/\Delta\nu]$. Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: 1982; p 96. For **1b**, T_c = 218 K and $\Delta\nu$ = 36.9 Hz. The spectrum of the free ligand (**5**) exhibits a similar temperature dependence from which a slightly **higher** barrier of $\Delta G_c^{\ddagger}$ = 54.5 kJ mol^{-1} may be calculated (T_c = 268 K, $\Delta\nu$ = 58.8 Hz).

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

(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 (×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 (×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 $CHCl_3$ (3 × 50 mL) and dried over Na_2SO_4. 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. ^{1}H NMR ($CDCl_3$): 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 (2*Z*,4*E*) isomer may also be identified.

(c) Preparation of 10. 5-Methoxy-2,4-pentadienal (1.0 g, 8.9 mmol) and $Fe_2(CO)_9$ (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}. ^{1}H NMR (C_6D_6): 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). ^{13}C NMR (CD_2Cl_2, -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}. ^{1}H NMR (C_6D_6): 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). ^{13}C NMR (CD_2Cl_2, -50 °C): δ 196.1 (C(1)), 52.1 (C(2)), 77.3, 80.0, 86.7 (C(3-5)), 20.7 (Me), 168.8 (CO_2Me), 205.5, 207.6 (CO_{basal}), 212.7 (CO_{axial}).

Table 5. Atomic Coordinates (×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 (×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)	-3247(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)

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}. ^{1}H NMR (C_6D_6): 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). ^{13}C NMR (CD_2Cl_2, -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 (CO_2Ph), 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 (NMe_2), 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). $[\alpha]_D$ (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 (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). $[\alpha]_D$ (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 OCOR (2.5 Hz) < OMe (4.1 Hz) < NR_2 (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-Me} = 6.3 Hz. $[\alpha]_D$ (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%). $[\alpha]_D$ (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 (NMe_2, s), 7.2–7.35 (Ph, m). Coupling constants are similar to those of **14a**. $[\alpha]_D$ (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%). $[\alpha]_D$ (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). $[\alpha]_D$ (CH_3CN, 1×10^{-3}): +272.

(f) Crystallographic Data. Data were collected on an Enraf-Nonius CAD4F diffractomer using Mo Kα 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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