Resolution, Racemization, and Epimerization in Acyclic (diene)Fe(CO)$_2$L and [(dienyl)Fe(CO)$_2$L]X Complexes (L = Phosphine, Phosphite)

James A. S. Howell,* Adrian D. Squibb, and Andrew G. Bell

Chemistry Department, Keele University, Keele, Staffordshire ST5 5BG, Great Britain

Patrick McArdle and Desmond Cunningham

Chemistry Department, University College, Galway, Ireland

Zeev Goldschmidt, Hugo E. Gottlieb, and Daphna Hezroni-Langerman

Chemistry Department, Bar Ilan University, Ramat Gan 52100, Israel

René Grée

Ecole Nationale Supérieure de Chimie de Rennes, Campus de Beaulieu, Avenue du Général Leclerc, 35700 Rennes, France

Received May 10, 1994[⊗]

A variety of substituted (2,4-pentadienal)-, (methyl 2,4-pentadienoate)-, and (3,5-heptadien-2-one)Fe(CO)$_2$L complexes have been prepared (L = PPh_3, $P(OMe)_3$, chiral phosphine); absolute configurations have been assigned by a combination of CD and single-crystal X-ray diffraction studies. The aldehyde and ketone complexes exhibit facile racemization or epimerization in solution (80–100 °C, benzene or toluene); the rates increase with increasing electron donor character of the 5-substituent, while diastereoface selectivity in the chiral phosphine series depends both on the phosphine and on the steric bulk of the 5-substituent. [(dienyl)Fe(CO)$_2$L]X salts also exhibit epimerization or racemization in solution. VT NMR studies have established axial/basal and s-cis/s-trans ratios in solution. For the aldehyde series, the correlation between the s-cis/s-trans ratio and the diastereoselectivity of nucleophilic attack (MeLi, MeMgI) has been examined. Crystal data: **14a**, orthorhombic, space group $P2_12_12_1$, a = 9.860(4) Å, b = 35.815(9) Å, c = 16.519(4) Å, Z = 4, R_1 = 0.0431 for 669 parameters and 8706 observed reflections; **15b**, monoclinic, space group $P2_1$, a = 8.7353(9) Å, b = 18.055(3) Å, c = 9.9894(11) Å, β = 113.395(8)°, Z = 2, R_1 = 0.0380 for 335 parameters and 4328 observed reflections; **17a**, orthorhombic, space group $P2_12_12_1$, a = 10.151(3) Å, b = 14.780(3) Å, c = 17.804(4) Å, Z = 4, R_1 = 0.0481 for 302 parameters and 1583 observed reflections; **23**, triclinic, space group $P\bar{1}$, a = 12.081(2) Å, b = 13.914(2) Å, c = 16.835(2) Å, α = 93.33(2)°, β = 109.47(2)°, γ = 113.18(2)°, Z = 4, R_1 = 0.0788 for 579 parameters and 9425 observed reflections.

A. Introduction

There is currently a resurgence of interest in acyclic (diene)Fe(CO)$_3$ complexes as organic intermediates,[1] perhaps best exemplified by the independent approaches of three groups to eicosanoid synthesis.[2] For asymmetric synthesis, the availability of homochiral complexes is of great importance; though biotransformation methods for kinetic resolution and desymmetrization have recently been reported,[3] most routes still rely on classical resolution using functional groups such as aldehyde,[4] ester,[5] or carboxylic acid.[6]

We have recently shown that substitution of CO by a homochiral phosphine ligand may also provide a means of resolution of planar chirality and, for complexes such as (tropone)Fe(CO)$_3$ where racemization is facile, may

* To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1994.

(1) For a review, see: Grée, R. *Synthesis* **1989**, 341.

(2) (a) Nunn, K.; Mosset, P.; Grée, R.; Saalfrank, R. W. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1188. (b) Franck-Neumann, M.; Colson, J. P. *Synlett* **1991**, 891. (c) Tao, C.; Donaldson, W. A. *J. Org. Chem.* **1993**, *58*, 2135.

(3) (a) Howell, J. A. S.; Palin, M. G.; Jaouen, G.; Top, S.; El Hafa, H.; Cense, J. M. *Tetrahedron: Asymmetry* **1993**, *4*, 1241. (b) Howell, J. A. S.; Palin, M. G.; Jaouen, G.; El Hafa, H.; Top, S. *Tetrahedron: Asymmetry* **1992**, *3*, 1355. (c) Alcock, N. W.; Crout, D. H. G.; Henderson, C. M.; Thomas, S. E. *J. Chem. Soc., Chem. Commun.* **1988**, 746.

(4) (a) Franck-Neumann, M.; Martina, D.; Heitz, M. P. *J. Organomet. Chem.* **1986**, *301*, 61. (b) Djedani, F.; Grée, D.; Martelli, J.; Grée, R.; Leroy, L.; Bolard, J.; Toupet, L. *Tetrahedron Lett.* **1989**, *30*, 3781.

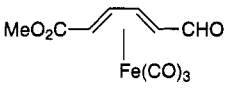
(5) Franck-Neumann, M.; Briswalter, C.; Chemla, P.; Martina, D. *Synlett* **1990**, 637.

0276-7333/94/2313-4336$04.50/0

also be used to control diastereoface selectivity.[7] We wish to report here our complete results on diastereoisomer separation and interconversion in the acyclic (diene)Fe(CO)$_2$L and [(dienyl)Fe(CO)$_2$L]X series.[8]

B. Results and Discussion

1. Racemization and Epimerization in the (diene)Fe(CO)$_2$L Series. Inversion of configuration in the (diene)Fe(CO)$_3$ series is a relatively high energy process, exemplified by the slow racemization of **1** at 119 °C ($k = 4 \times 10^{-6}$ s^{-1}).[9]

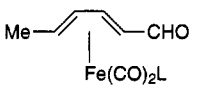


1

By suitable substitution on the diene and on the metal center, the rates of racemization can be enhanced, and equivalent facile epimerization in complexes containing homochiral phosphine ligands provides some control over diastereofacial selectivity.

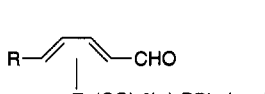
(a) Synthesis and Absolute Configuration. The complexes studied may be divided into three categories.

(i) The first is the (sorbaldehyde)Fe(CO)$_2$L series **2**–**9**, in which the rate of racemization or epimerization and diastereofacial selectivity has been investigated as a function of the ligand L (Men = menthyl).



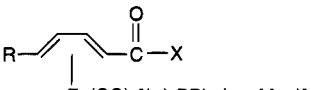
complex	L
2	CO
3	PPh_3
4	$P(OMe)_3$
5	(+)-PPh_2(neoMen)
6	(–)-PPh_2(Men)
7	(–)-PPh_2(OMen)
8	(+)-P(o-anisyl)PhMe

(ii) The second is the (2,4-pentadienal)Fe(CO)$_2$L series **5** and **9**–**13**, in which the rates of epimerization and diastereofacial selectivity have been investigated as a function of the 5-substituent.



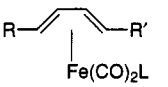
complex	R
5	Me
9	CO_2Me
10	H
11	Ph
12	$PhCO_2$
13	OMe

(iii) The third is the series **5** and **14**–**16**, in which the rate epimerization and diastereofacial selectivity have been investigated as a function of the nature of the α-carbonyl functionality.



complex	R	X
5	Me	H
14	Me	OMe
15	H	OMe
16	Me	Me

(2-methyl-1,3-butadiene)Fe(CO)$_2$[(+)-PPh_2(neoMen)] (**17**) has been prepared as an example of a simple alkyl-substituted complex, and in addition, some racemic complexes containing achiral ligands have been prepared as an aid to solution structure elucidation.



complex	R	R′	L
18	H	CO_2Me	PPh_3
19	H	CHO	PPh_3
20	$PhCO_2$	CHO	PPh_3
21	OMe	CHO	PPh_3
22	Me	CHO	PPh_2OMe
23	Me	COMe	PPh_3
24	CO_2Me	CHO	PPh_3
25	Me	CO_2Me	PPh_3

All phosphine and phosphite complexes were prepared from the tricarbonyl by reaction with ligand in the presence of Me_3NO.[10] Such substitution using a homochiral ligand renders the enantiomeric pair of complexes diastereoisomeric. At the temperature and time scale of the reaction, no diastereoisomer interconversion occurs, and both diastereoisomers are isolated in equimolar amounts when the reaction is allowed to proceed to completion.

All diastereoisomeric complexes except **8**, **9**, and **17** were separable by prepaqrative TLC and are designated **a** and **b** in order of elution. A diastereoisomerically pure sample of **8**, an enriched sample of **9**, and enantiomerically pure samples of **3** and **4** were obtained by reaction of the appropriate ligand with the homochiral or enriched tricarbonyls. A single diastereoisomer of **17** was isolated in high purity by fractional recrystallization.

Absolute configurations have been assigned to all complexes using a combination of CD spectroscopy and crystal structure determinations of the three complexes **14a**, **15b**, and **17a** (Figure 1). The configuration established for **14a** is 2*S*. For a series of similar complexes, it has been shown that a correlation exists between the sign of the CD bands due to d–d transitions at long wavelength and their absolute configuration.[4b] Thus, the spectra of the aldehyde, ketone, and ester analogues **5a**, **14a**, and **16a** are essentially similar; that of **16b** is almost mirror image to that of **16a**, indicating that the chiral phosphine hardly perturbs these long-wavelength

(6) (a) Birch, A. J.; Kelly, L. F.; Weerasuria, D. V. *J. Org. Chem.* **1988**, *53*, 278. (b) Musco, A.; Paiaro, G.; Palumbo, R. *Chim. Ind. (Milan)* **1968**, *50*, 669.

(7) Howell, J. A. S.; Squibb, A. D.; Goldschmidt, Z.; Gottlieb, H. E.; Almadhoun, A.; Goldberg, I. *Organometallics* **1990**, *9*, 80.

(8) For preliminary communications, see: (a) Howell, J. A. S.; Squibb, A. D.; Walton, G.; McArdle, P.; Cunningham, D. *J. Organomet. Chem.* **1985**, *319*, C45. (b) Howell, J. A. S.; Tirvengadum, M. C.; Squibb, A. D.; Walton, G.; McArdle, P.; Cunningham, D. *J. Organomet. Chem.* **1988**, *347*, C5.

(9) Whitlock, W. H.; Markezich, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 5290.

(10) Birch, A. J.; Kelly, L. F. *J. Organomet. Chem.* **1985**, *268*, C5.

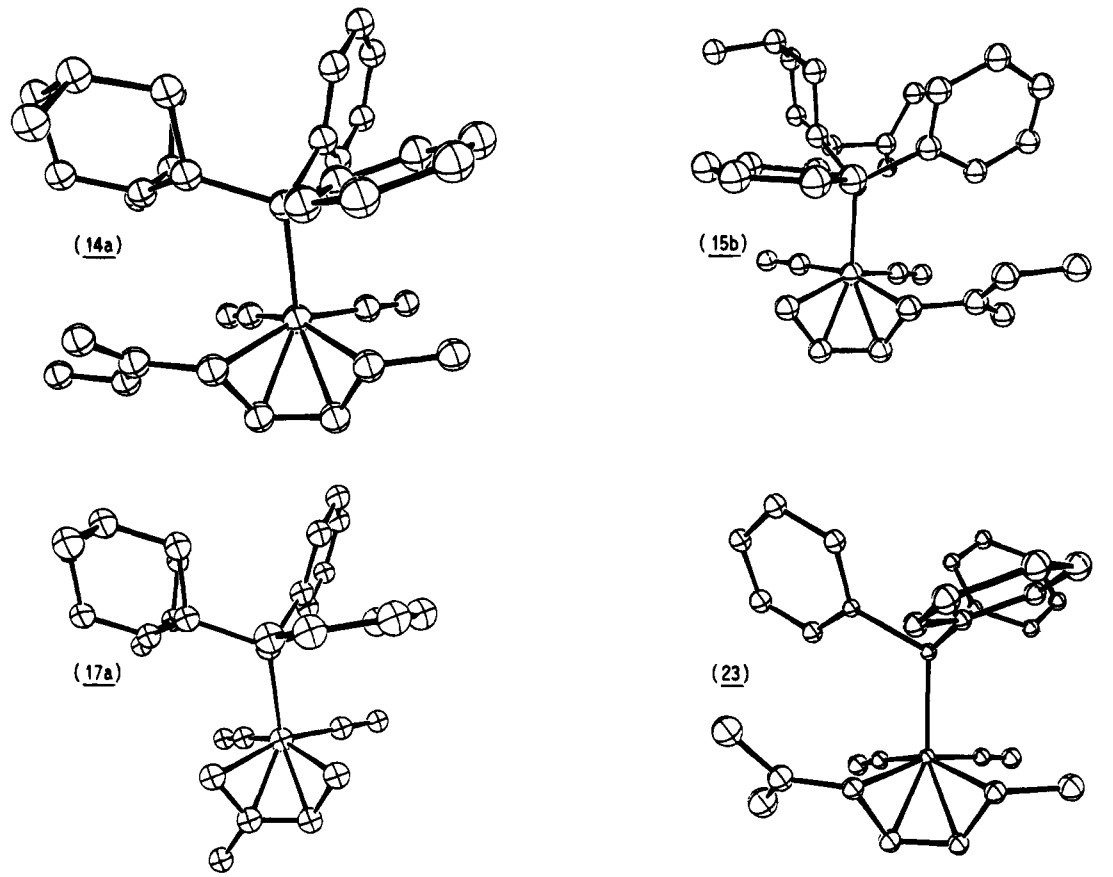


Figure 1. Molecular Structures of **14a**, **15b**, **17a**, and **23**.

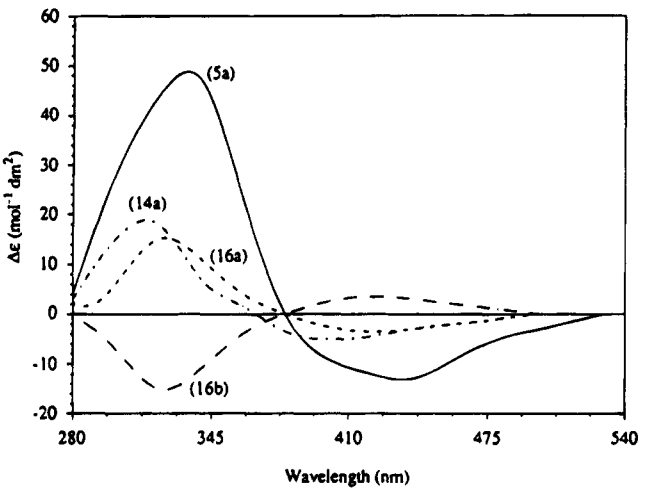


Figure 2. CD spectra of **14a**, **5a**, and **16a,b**.

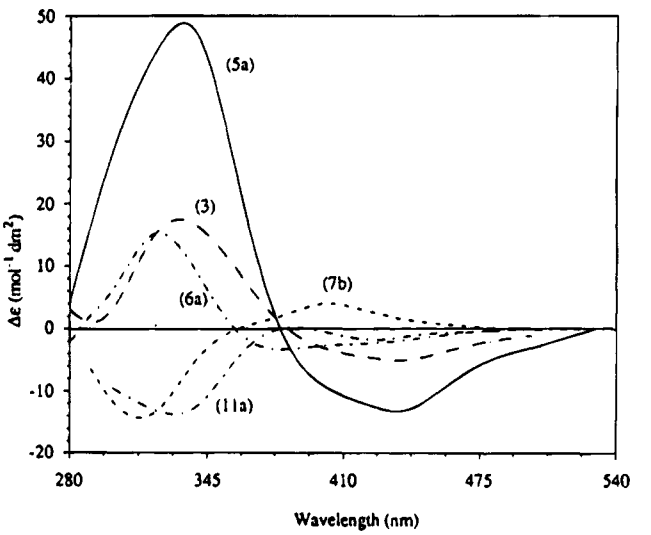
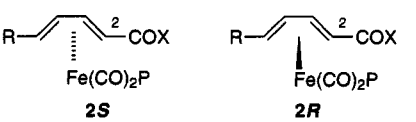


Figure 3. CD spectra of **3**, **5a**, **6a**, **7b**, and **11a**.

bands (Figure 2). Absolute configurations in the aldehyde series **6**, **7**, and **11** as well as the homochiral PPh_3 complex **3** may be assigned by comparison with **14a** (Figure 3). Configurations of the electron-donor complexes **12** and **13** were assigned by comparison to the spectra of the tricarbonyls of known 2*S* configuration[11] (Figure 4). CD spectra of the monosubstituted complexes **10b** and **15b** (Figure 5) are ambiguous, showing a relatively ill-defined absorption at longer wavelength, though the shorter wavelength band at 300 nm is indicative of the 2*S* configuration. This has been confirmed by a crystal structure determination of **15b** (Figure 1). Thus, in all cases, the first diastereoisomer eluted on chromatography has the 2*S* configuration.



A crystal structure determination of the single diastereoisomer of (2-methyl-1,3-butadiene)$Fe(CO)_2$[(+)-PPh_2(neoMen)] (**17a**) isolated by fractional recrystallization reveals a 2*R* absolute configuration (Figure 1). The positive absorption at 380 nm in the CD spectrum of **17a** (Figure 5) is consistent with spectra of (2*S*)-(2-

(11) Howell, J. A. S.; Bell, A. G.; O'Leary, P. J.; McArdle, P.; Cunningham, D.; Stephenson, G. R.; Hastings, M. *Organometallics* **1994**, *13*, 1806.

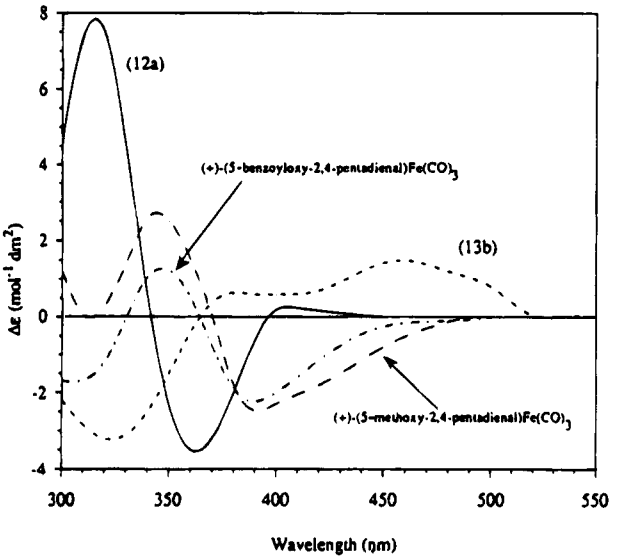


Figure 4. CD spectra of **12a** and **13b** and their corresponding tricarbonyls.

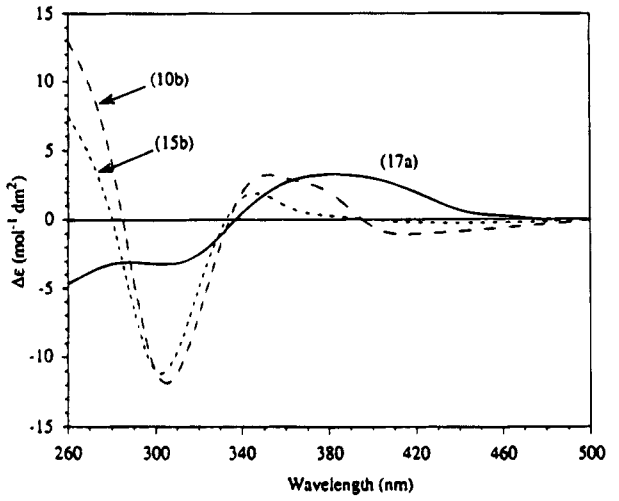


Figure 5. CD spectra of **10b**, **15b**, and **17a**.

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

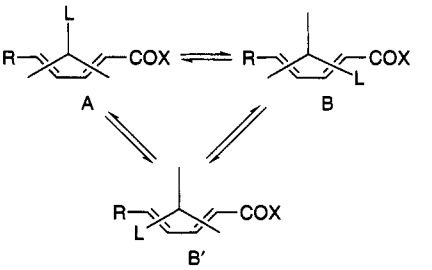
	14a	15b	17a	23
Fe—CO (av)	1.723(10)	1.774(5)	1.743(11)	1.76(4)
Fe—P	2.262(2)	2.241(9)	2.235(3)	2.248(8)
Fe—C_{inner} (av)	2.045(9)	2.044(5)	2.057(10)	2.051(4)
Fe—C_{outer} (av)	2.171(9)	2.114(5)	2.079(10)	2.145(4)
CO—Fe—CO	87.6(4)	92.6(2)	91.9(6)	86.5(2)
CO—Fe—P (av)	101.2(3)	100.9(8)	101.4(3)	102.1(12)
P1—P2[a]	28	25		31
Fe—P—C_{ipso}—C_α	−78	−82	79	
	18	23	28	

[a] P1 = plane of diene; P2 = plane of CO_2Me or COMe.

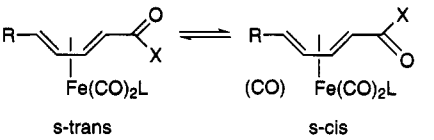
methyl-1,3-butadiene)Fe(CO)$_3$[12] and (2*R*)-(1,3-butadiene-2-carboxylic acid)Fe(CO)$_3$[3c] isolated by classical and biochemical resolution methods, respectively.

Several structural features of **14a**, **15b**, and **17a** are worthy of comment. The geometries (Table 1) are typical of the pseudo-square-pyramidal coordination adopted by (diene)Fe(CO)$_3$ complexes. The phosphine adopts the axial position of the square pyramid, though in solution, basal isomers are substantially populated for **15b** and **17a** (vide infra). The phosphine is oriented so as to present a "flat" benzene ring toward the diene bite angle, slightly twisted towards C4 in all cases. As **14a** and **15b** are of opposite planar chirality, this means that the neomenthyl group is moved into closer proximity to the ester function in **14a** as compared to **15b**. Indeed, the ester conformations are oppsite, being s-trans in **14a** but s-cis in **15b**. Such differential interactions may provide the origins of both differences in diastereoisomer stability and differences in the axial/basal and s-cis/s-trans ratio observed between diastereoisomers (vide infra). The ester groups in **14a** and **15b** are twisted from coplanarity with the diene by 28 and 25°, respectively.

(b) Solution Structure and Fluxionality. For the majority of the aldehyde, ketone, and ester complexes, two fluxional processes are apparent. At higher temperature (≥ −60 °C), exchange is evident between the three geometric isomers resulting from occupancy of the axial (A) or basal (B/B′) sites of the square pyramid.



At lower temperatures (−110 to −60 °C), spectral changes may be attributed to restriction of C—COX rotation between s-cis and s-trans conformations in some or all of the geometric isomers present.



Complexes **6a,b** may be taken as an example of the NMR spectral analysis used (Figure 6). Thus, for **6b** the broadened ^{31}P resonances at 25 °C are replaced by two sharpened resonances at −60 °C in a ratio of 6.5:1, which are assigned to axial and basal isomers, respectively, on the basis of the ^{13}CO subspectrum, which shows two resonances assignable to the nonequivalent basal CO pair. The minor basal isomer is not seen in the ^{13}CO subspectrum, and assignment to B or B′ is arbitrary. Further cooling to −100 °C results in sharpening of the minor basal resonance and a broadening and resolution of the major axial resonance into two peaks in a ratio of 1.2:1. The ^{1}H CHO subspectrum at −105 °C is also resolved into three resonances. The minor resonance is assigned to the minor basal isomer in purely the s-trans conformation (J_{12} = 7.1 Hz), while the major doublet (J_{12} = 7.6 Hz) and singlet ($J_{12} \leq 2$ Hz) resonances are assigned to a 1.2:1 mixture of the s-trans and s-cis conformers of the axial phosphine isomer.[13] Variable-temperature spectra of the diastereoisomer **6a** show only resonances due to the axial

(12) Kappes, D.; Gerlach, H.; Zbinden, P.; Dobler, M.; Konig, W. A.; Krebber, R.; Wenz, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1657.

(13) Values of $J_{12} \approx 8$ and ≤2 Hz for s-trans and s-cis conformations are consistent with NMR studies of acrolein: (a) Douglas, A. W.; Goldstein, J. H. *J. Mol. Spectrosc.* **1965**, *16*, 1. (b) Courtieu, J.; Gounelle, Y.; Gonard, P.; Kan, S. K. *Org. Magn. Reson.* **1974**, *6*, 151. (c) Davies, J. E. D. *J. Mol. Spectrosc.* **1969**, *29*, 499.

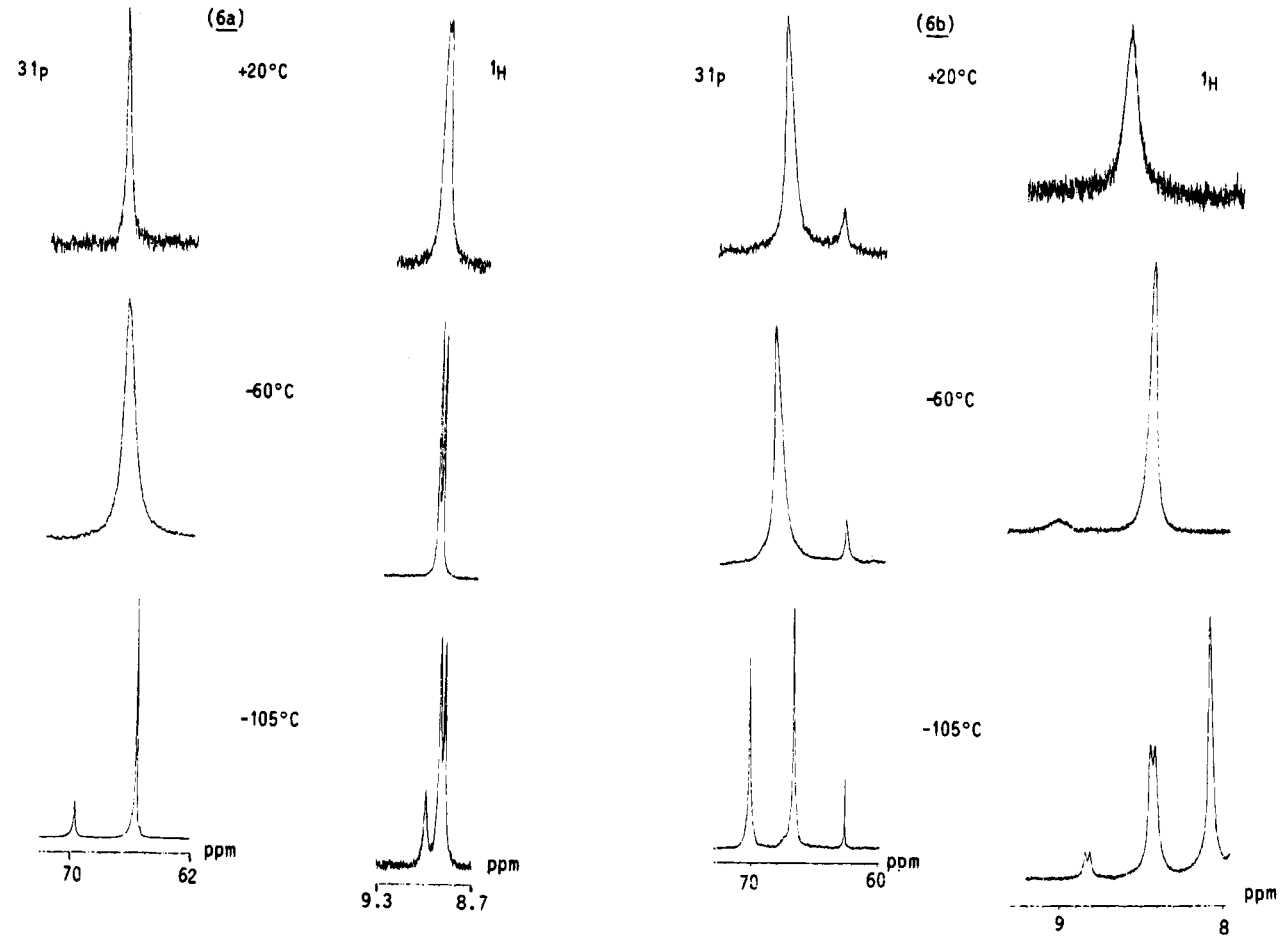


Figure 6. Variable-Temperature NMR Spectra of **6a,b** (CD_2Cl_2).

isomer at −60 °C, which are resolved into a 4.3:1 ratio of s-trans (J_{12} = 8.0 Hz) and s-cis ($J_{12} \leq$ 2Hz) at −105 °C. The averaged coupling constant at 0 °C (6.1 Hz) is lower than that predicted (6.9 Hz) on the basis of intensities and coupling constants in the low-temperature spectrum, thus indicating a slight increase in population of the less stable s-cis conformer with increasing temperature. Nevertheless, averaged room-temperature coupling constants provide an accurate qualitative guide to the predominant aldehyde conformation present in solution.

Several of the ketone- and ester-substituted complexes also exhibit low-temperature ^{31}P spectra which are consistent with restricted C—C(O)X bond rotation. For example, the spectrum of **15a** (Figure 7) is resolved into three resonances at −30 °C, assignable to populations of A and B/B′ geometric isomers. When the temperature is lowered to −110 °C, two of the three resonances are additionally resolved into pairs, indicative of restriction of s-cis ⇌ s-trans interconversion. The major isomers are assigned as s-cis on the basis of the crystal structure of **15b**, which shows an s-cis geometry. Solution assignments of the major conformational isomers of **25**, **14a,b**, **23**, and **16a,b** are made similarly on the basis of the observed solid-state structures of **14a** and **22** (vide infra). Complete data for axial/basal and s-cis/s-trans distributions are given in Table 2.

Several general features are apparent.

(i) As in simple alkyl-substituted complexes,[14] trans-terminal disubstitution of the diene favors population of the axial isomer A. Only for the monosubstituted complexes **10**, **15**, **17**, **19**, and complexes **13** and **21**, containing the sterically nondemanding OMe substituent, can significant concentrations of basal isomers be detected. In the diastereoisomer pairs containing chiral phosphines, there is generally a greater population of the basal isomer in the diastereoisomer of 2*R* planar chirality.

(ii) In the aldehyde series, replacement of CO by a phosphine results in an increased population of the s-trans conformation in all cases, as indicated by the averaged J_{12} values compared to those of the tricarbonyl. In all cases of complexes containing homochiral ligands, the s-trans conformer is preferentially populated in the diastereoisomer of 2*S* planar chirality.

Only in the case of complex **21** are all three axial/basal isomers and s-trans/s-cis conformers sufficiently populated to warrant a precise line-shape analysis. Experimental and simulated ^{31}P spectra are shown in Figure 8, and kinetic parameters are tabulated in Table 3. Assignment of the major isomer to A follows from the ^{13}C spectrum at −50 °C, which shows two sharp phosphorus-coupled basal CO resonances at 211.3 and 213.9 ppm. The other assignments provide the best agreement with the observed room-temperature J_{12} value of 5.9 Hz, though the assignment to B and B′ is again arbitrary.

The results demonstrate a barrier to s-cis/s-trans exchange of 36 kJ mol^{-1} in both the A and B′ isomers.

(14) Howell, J. A. S.; Walton, G.; Tirvengadum, M. C.; Squibb, A. D.; Palin, M. G.; McArdle, P.; Gottlieb, J.; Strul, G. *J. Organomet. Chem.* **1991**, *401*, 91.

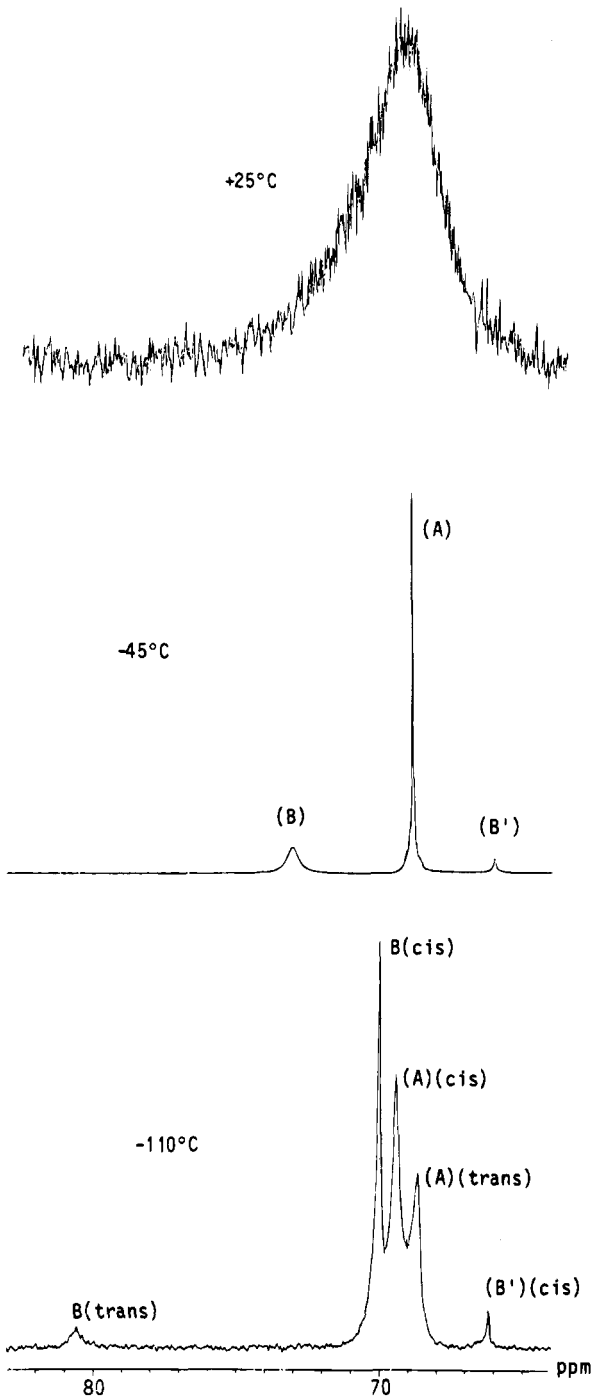


Figure 7. Variable-Temperature ^{31}P NMR Spectra of **15a** (CD_2Cl_2).

Most interestingly, there is a clear lowering of the barrier to B′ → B exchange (40 kJ mol^{-1}) compared to that for A → B or A → B′ exchange (53 kJ mol^{-1}). These results provide support for our previously reported molecular orbital analysis of this fluxional process.[15]

(c) Thermal Epimerization and Racemization. Rates and equilibrium constants for epimerization in benzene-d_6 or toluene-d_8 were measured by in situ integration of the ^{1}H formyl resonances for the aldehyde diastereoisomer pairs. The inner diene resonance H_3 was used to monitor epimerization of the ketone diastereoisomer pair **16a,b**. Racemization of homochiral samples of complexes **2**–**4** was monitored by analysis of aliquots in the presence of chiral shift reagent.[16] This provides good separation of the enantiomeric formyl resonances for complexes **2** and **3** and good separation of the enantiomeric P(OMe)$_3$ doublets for complex **4**.

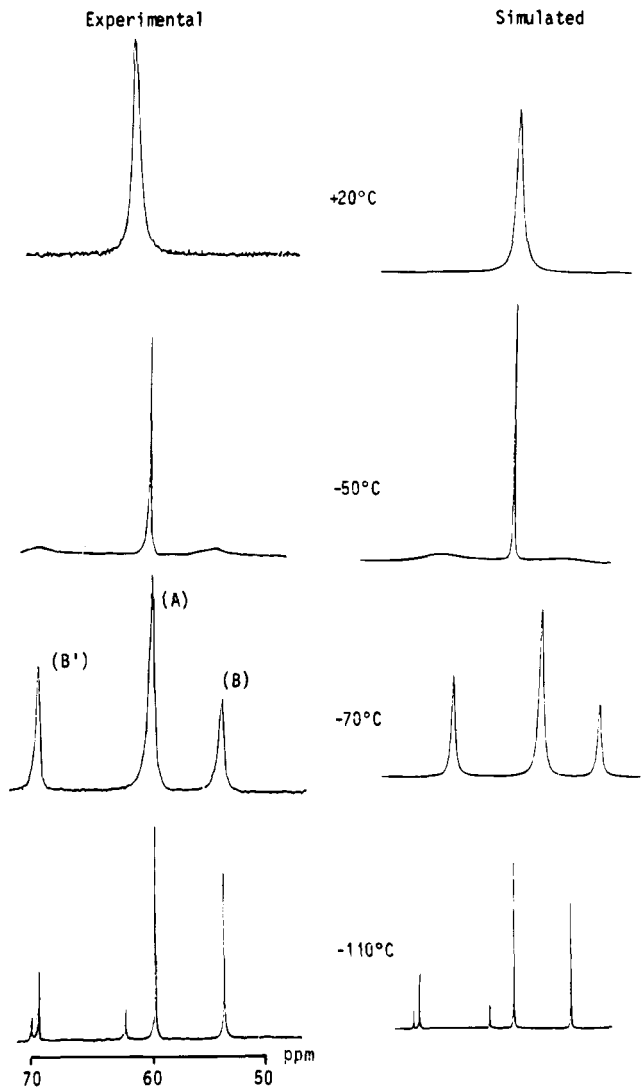
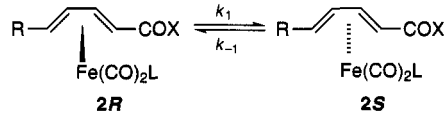


Figure 8. Experimental and Simulated ^{31}P NMR Spectra of **21** (CD_2Cl_2).



2R **2S**

Plots of $\ln[(P_\infty/P_t)/P_t + 1)]$, where P is the ratio of diastereoisomers or enantiomers, against time[17] give straight lines whose gradient is equal to $-(k_1 + k_{-1})$; correlation coefficients of 0.994 or greater were obtained in all cases. The results are summarized in Table 4.

Several points may be noted.

(i) In the (sorbaldehyde)Fe(CO)$_2$L series, the tricarbonyl- and P(OMe)$_3$-substituted complexes are inert to racemization under conditions where the PPh$_3$ and chiral phosphine complexes undergo smooth racemiza-

(15) Howell, J. A. S.; Bell, A. G.; Cunningham, D.; McArdle, P.; Albright, T. A.; Goldschmidt, Z.; Hezroni-Langerman, D. *Organometallics* **1993**, *12*, 2541.

(16) The shift reagent used in all studies was tris[3-((heptafluoropropyl)hydroxymethylene)-(+)-camphorato]europium(III).

(17) Dixon, D. T.; Kola, J. C.; Howell, J. A. S. *J. Chem. Soc., Dalton Trans.* **1984**, 1307.

Table 2. NMR Spectroscopic Data for Axial/Basal and s-cis/s-trans Ratios

			K = [s-cis]/[s-trans]		
complex	J_{12}[a]	ratio A:B:B′ [b]	A	B	B′
3	5.6 (3.7)	32:1:0 (64.0, 58.8)	0.50	trans only	
4	6.1 (3.7)	22:4:1 (183.3, 181.9, 182.9)	0.15	trans only	
5a	7.8 (3.7)	60:1:0 (65.5, 60.2)	0.05	trans only	
5b	5.1 (3.7)	32:1:0 (66.4, 61.7)	0.66	1.0	
6a	7.1 (3.7)	1:0:0 (66.6)	0.22		
6b	4.5 (3.7)	6:1:0 (67.7, 62.5)	0.50	trans only	
8a	6.7 (3.7)	1:0:0 (36.8)	0.05		
22	5.6 (3.7)	40:1:0 (170.7, 166.8)	0.66	trans only	
7a	5.6 (3.7)	50:1:0 (164.5, 154.5)	*d*	*d*	
7b	5.3 (3.7)	50:1:0 (162.7, 160.0)	*d*	*d*	
24	5.5 (2.9)	1:0:0 (61.1)	1.0		
9b	4.4 (2.9)	11:1:0 (62.0, 59.6)	4.3	*c*	
19	4.7 (3.4)	1:4.8:0 (68.1, 74.3)	1.0	0.76	
10a	6.5 (3.4)	4:1:0 (68.0, 73.2)	0.45	*c*	
10b	4.9 (3.4)	30:30:1 (67.5, 71.7, 64.6)	0.16	6.8	*c*
11a	5.6 (3.4)	40:1:0 (63.3, 55.8)	1.6	*c*	
11b	4.2 (3.4)	40:1:0 (61.9, 59.5)	17	*c*	
20	3.9 (2.5)	5.5:1:0 (61.8, 68.1)	1.7	*d*	
12a	5.6 (2.5)	1.0:0:0 (65.0)	1.0		
12b	br (2.5)	1.0:0:0 (65.2)	*d*		
21	6.4 (4.1)	1.9:1.1:1.0 (61.2, 55.0, 70.5)	0.16	cis only	0.57
13a	6.6 (4.1)	29:8.0:1.0 (65.6, 70.5, 56.3)	trans only	0.31	cis only
13b	br (4.1)	12:2.3:1.0 (66.9, 69.9, 55.5)	1.0	0.20	cis only
18		1:5:0 (69.6, 74.3)	*c*	cis only	
15a		12:4:1 (68.9, 73.1, 66.0)	17	1.4	cis only
15b		4.2:1.6:1.0 (70.1, 71.5, 68.9)	*d*	*d*	1.0
25		1:0:0 (65.5)	trans only		
14a		34:1:0 (68.7, 63.2)	0.07	*c*	
14b		40:1:0 (68.8, 63.3)	0.03	*c*	
23		1:0:0 (63.2)	cis		
16a		12:1:0 (65.3, 60.1)	13	cis only	
16b		1:0:0 (67.3)	cis only		
17a		1:1.5:0 (69.7, 76.1)			
31		0:1:0 (60.5)			
32		5:95:0 (152.4, 153.6)			
33a		0:1:0 (60.9)			

[a] J_{12} values in Hz at 20−60 °C in C_6D_6; values for the tricarbonyl species in parentheses. [b] The B/B′ assignment is arbitrary; ^{31}P chemical shifts in ppm at −40 to −60 °C are given in parentheses. [c] Ratio not established unambiguously. [d] Resonances broadened but not resolved at −110 °C.

Table 3. Kinetic Data and Activation Parameters for Axial/Basal and s-cis/s-trans Exchange in 21

T (K)	k_{CTA}[a] (s^{-1})	k_{CTB}[b] (s^{-1})	$k_{B'B}$[c] (s^{-1})	k_{AB}[d] (s^{-1})	$k_{AB'}$[e] (s^{-1})	$\Delta G^{\ddagger}_{CTA}$ (kJ mol^{-1})	$\Delta G^{\ddagger}_{CTB'}$ (kJ mol^{-1})	$\Delta G^{\ddagger}_{B'B}$ (kJ mol^{-1})	$\Delta G^{\ddagger}_{AB}$ (kJ mol^{-1})	$\Delta G^{\ddagger}_{AB'}$ (kJ mol^{-1})
173	50	60				35.9	35.6			
183	170	200				36.2	35.9			
193	650	1000	90			36.1	35.5	39.3		
203	1600	3060[f]	220			36.6		39.9		
213	4500	9150[f]	500			36.6		40.5		
223	1.0×10^4[f]	2.5×10^4[f]	1800					40.1		
233	2.3×10^4[f]	6.2×10^4[f]	4000[f]							
243	4.9×10^4[f]	1.4×10^5[f]	9400[f]							
253	9.7×10^4[f]	3.1×10^5[f]	2.0×10^4[f]	43	60			40.7	53.7	52.9
263	1.8×10^5[f]	6.4×10^5[f]	4.0×10^4[f]	100	150			40.9	54.0	53.1
273	3.3×10^5[f]	1.3×10^6[f]	7.5×10^4[f]	225	350				54.3	53.3
283	5.7×10^5[f]	2.3×10^6[f]	1.2×10^5[f]	900	1500				53.1	51.9
293	9.6×10^5[f]	4.2×10^6[f]	2.4×10^5[f]	1630	2800				53.6	52.3

[a] Rate constant for s-cis → s-trans exchange in axial isomer (A). [b] Rate constant for s-cis → s-trans exchange in basal isomer (B′). [c] Rate constant for B′ → B exchange. [d] Rate constant for A → B exchange. [e] Rate constant for A → B′ exchange. [f] Extrapolated.

tion and epimerization. Throughout the series **5**−**8** the most stable diastereoisomer retains the 2*S* planar configuration, even when the configuration of the C1 menthyl center is inverted in the cases of **5** and **6**. The diastereoface selectivity for **7** and **8**, in which the asymmetry of the ligand is placed further from and closer to the metal center, respectively, suggests that diastereoisomer stability is determined by a fine balance of diene substituent−ligand substituent interactions.

(ii) The rate of epimerization in the (2,4-pentadienal)-$Fe(CO)_2L$ series is extremely sensitive to the nature of the 5-substituent, increasing in the order CO_2Me (inert) < H < Me < Ph ≈ OCOPh < OMe. The rate thus increases with the increasing electron-donor nature of the 5-substituent. In contrast, diastereoface selectivity seems to be maximized mainly by the steric bulk of the 5-substituent in the order H < Ph < OMe ≈ OCOPh < Me.

(iii) Facile epimerization is observed only in the aldehyde series and the ketone complex **16** and is not observed in the ester derivatives **14** and **15** or the isoprene complex **17**. The ketone complex exhibits a faster rate of epimerization but a poorer diastereoface selectivity relative to its aldehyde analogue.

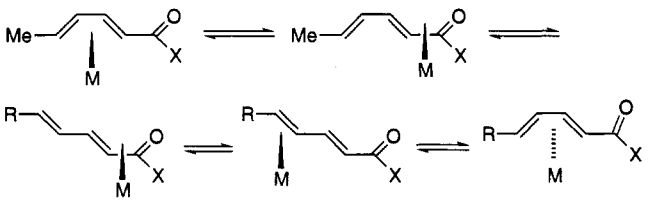
A mechanism which is consistent with these observations is given in Scheme 1.

Table 4. Rate and Equilibrium Constants for Racemization and Epimerization

complex	solvent	T (K)	k_1 (10^5 s^{-1})	k_{-1} (10^5 s^{-1})	K
2	C_6D_6	80		no racemizn	
3	C_6D_6	80		no racemizn	
4	C_6D_6	80	2.7	2.7	1.0
5	C_7D_8	95	7.0	2.0	3.5
6	C_6D_6	75	17.7	7.7	2.5
7	C_7D_8	95	7.4	7.4	1.0
8	C_7D_8	100	0.9	0.9	1.0
9	C_7D_8	100		no epimerizn	
10	C_7D_8	100	2.4	2.4	1.0
11	C_6D_6	75	3.1	2.3	1.3
12	C_7D_8	95	10.5	10.5	1.0
13	C_6D_6	70	18.5	11.5	1.6
14	C_6D_6	80		no epimerizn	
15	C_6D_6	80		no epimerizn	
16	C_6D_6	75	12.1	7.1	1.7
17	C_7D_8	100		no epimerizn	
30	acetone-d_6	55		no racemizn	
31	$CDCl_3$	55	4.4	4.4	1.0
32	$CDCl_3$	55	7.4	7.4	1.0
33	$CDCl_3$	50	70	50	1.4
33	$CDCl_3$[a]	50	82	58	1.4

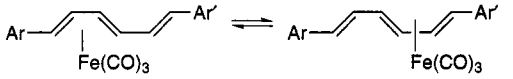
[a] Cation generated in situ by addition of 25 M excess of trifluoroacetic acid.

Scheme 1



X = H, Me

The formal diene—Fe inversion is postulated to proceed by stepwise 1,3-metal shifts which yield initially an η^4-enone intermediate. Though (enone)Fe(CO)$_2$L complexes of α,β-unsaturated aldehydes and ketones are well established,[18] α,β-unsaturated ester complexes are unknown. Molecular orbital studies have shown that replacement of CO by phosphine serves to stabilize the metal—enone interaction by rendering the Fe(CO)$_2$L moiety a better donor to the enone π_3 orbital.[19] The electronic character of the aryl substituent has been shown[20] to be important in determining rates of bond shift isomerization of the type The magnitude of the



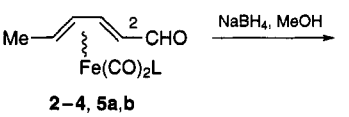
effects observed is, however, much less than that described in the present work. Ease of access to the required s-cis aldehyde conformer may also affect the rate; thus, complex **6a** with a cis/trans ratio of 0.22 at low temperature undergoes epimerization about 16 times as fast as **5a**, where the cis/trans ratio observed at low temperature is only 0.05.

The kinetic measurements do not distinguish between the mechanism proposed in Scheme 1 and a dissociative mechanism in which inversion of planar configuration is accomplished by complete dissociation and recoordination of the diene, and it may be noted that small amounts of (diene)Fe(CO)$_3$ complex and the free diene ligand are detected by NMR in most epimerization studies. In the worst case, complex **11a,b**, these amounts reach 10% and 4%, respectively. Experiments using **11a** clearly suggest that these products arise from an independent decomposition pathway initiated by metal-phosphorus bond cleavage.

(i) The amount of decomposition can be suppressed by 50% if epimerization is carried out in the presence of a 5 M excess of (+)-PPh$_2$(neoMen), though the rate of epimerization is unaffected, (ii) Decomposition to give free ligand is completely suppressed if epimerization is carried out under 1 atm of CO, though the rate of epimerization is unaffected. The mechanism of decomposition can thus be represented as in Scheme 2.

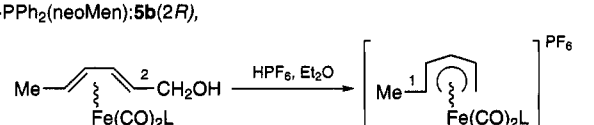
The tricarbonyl is inert to thermal decomposition or phosphine substitution to regenerate **11a,b** at the temperature of the epimerization. NMR analysis of the tricarbonyl isolated after epimerization had reached equilibrium showed an enantiomer ratio of 1.4:1, thus mirroring the thermodynamic ratio of **11a,b** and suggesting an essentially equal rate of decomposition of both diastereoisomers.

2. Racemization and Epimerization in the [(dienyl)Fe(CO)$_2$L]X Series. Reduction of the α-carbonyl group followed by protonation provides a route to synthetically useful [(dienyl)Fe(CO)$_2$L]X salts. We have accordingly prepared the complexes below, derived from the (sorbaldehyde)Fe(CO)$_2$L series, to examine the possibility of an equivalent racemization or epimerization in the dienyl series.



2–4, 5a,b

L = CO:**2**(2*S*),
L = PPh$_3$:**3**(2*S*),
L = P(OMe)$_3$:**4**(2*S*),
L = (+)-PPh$_2$(neoMen):**5a**(2*S*),
L = (+)-PPh$_2$(neoMen):**5b**(2*R*),



26–28, 29a,b	**30–32, 33a,b**
26	**30** (1*R*)
27	**31** (1*R*)
28	**32** (1*R*)
29a	**33a** (1*R*)
29b	**33b** (1*S*)

Homochiral samples of complexes **30–33** were prepared from the homochiral (sorbaldehyde)Fe(CO)$_2$L complex. The absolute configurations shown are based on the known configurations of the starting aldehyde complex; CD spectra (Figure 9) show the *same* sign of the long-wavelength transition observed for the starting

(18) For recent references, see: (a) Vichi, E. J. S.; Fujiwara, F. Y.; Stein, E. *Inorg. Chem.* **1985**, *24*, 286. (b) Bender, B. R.; Koller, M.; Linden, A.; Marcuzzi, A.; von Philipsborn, W. *Organometallics* **1992**, *11*, 4628. (c) Marcuzzi, A.; Linden, A.; Rentsch, D.; von Philipsborn, W. *J. Organomet. Chem.* **1992**, *429*, 87. (d) Thomas, S. E.; Richards, C. J.; Saberi, S. P.; Hill, L. *Pure Appl. Chem.* **1992**, *64*, 371. (e) Hill, L.; Richards, C. J.; Thomas, S. E. *Pure Appl. Chem.* **1990**, *62*, 2057. (f) Cherkaoui, H.; Martelli, J.; Greé, R. *Tetrahedron Lett.* **1991**, *32*, 7259.

(19) Calhorda, M. J.; Vichi, E. J. S. *Organometallics* **1990**, *9*, 1060.

(20) Whitlock, H. W.; Reich, C. R.; Woessner, W. D. *J. Am. Chem. Soc.* **1971**, *93*, 2483.

(21) For similar arguments regarding the protonation of (butadiene)-Fe(CO)$_3$, see: (a) Brookhart, M.; Whitesides, T. H.; Crockett, J. M. *Inorg. Chem.* **1976**, *15*, 1550. (b) Whitesides, T. H.; Arhart, R. W. *Inorg. Chem.* **1975**, *14*, 209. (c) Brookhart, M.; Harris, D. L. *Inorg. Chem.* **1974**, *13*, 154.

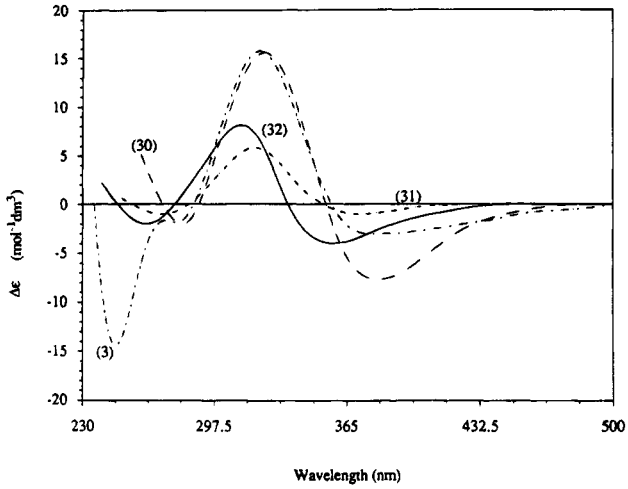
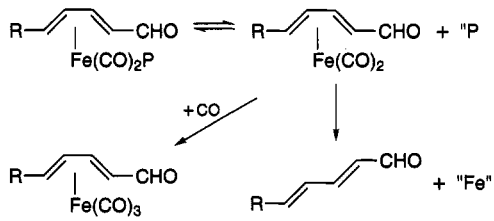
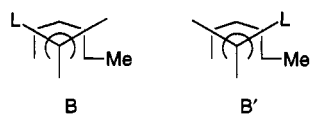


Figure 9. CD spectra of **3** and **30–32**.

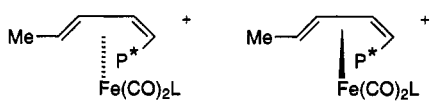
Scheme 2



aldehyde complex. In contrast to the neutral diene complexes, NMR studies (Table 2, Experimental Section) show almost exclusive population of a single basal site by the phosphine ligand; B rather than B′ seems most likely for steric reasons.



Racemization in complexes **30–32** was monitored by addition of excess (+)-PPh_2(neoMen) (P*) to aliquots withdrawn from heated acetone or dichloromethane solutions. Such addition generates the pair of diastereoisomeric phosphonium adducts **34a,b**, which can easily be distinguished by separated ^{31}P resonances in the chemical shift range of 30–32 ppm.



Epimerization of **33b** was monitored by the appearance of a second resonance at 65.8 ppm assignable to **33a**.

No racemization of the tricarbonyl **30** was observed. Complexes **31** and **33b** did racemize and epimerize respectively (Table 3), though decomposition was also substantial (ca. 40%) during the time taken to reach thermodynamic equilibrium. Though the rate of epimerization of **33** is much enhanced, the diastereoface selectivity is poor relative to its aldehyde precursor **5**. Racemization of the phosphite complex **32** proceeds smoothly with only a trace of decomposition, in contrast to the aldehyde precursor **4**, where no racemization is observed.

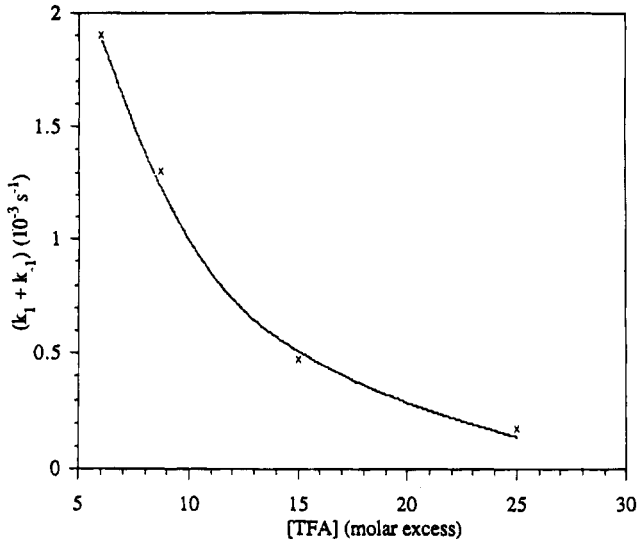
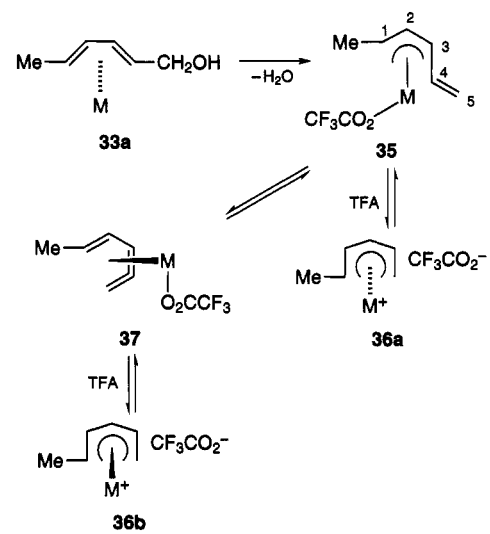


Figure 10. Effect of [TFA] on the Rate of Epimerization of **33b** ($CDCl_3$).

Scheme 3[a]

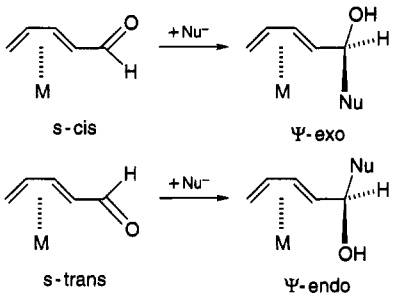


[a] M = $Fe(CO)_2L$.

A similar rate of epimerization of **33** is observed when the cation is generated in situ in $CHCl_3$ in the presence of a large excess of trifluoroacetic acid. The rate, however, is surprisingly *inversely* proportional to acid concentration (Figure 10). These results seem best accommodated by the mechanism in Scheme 3, in which initial protonation yields the neutral η^3-allyl trifluoroacetate complex **35**, which is ionized to the η^5-pentadienyl cation **36a** in the presence of excess acid. Epimerization occurs preferentially through **35** via a metal shift and C3—C4 bond rotation to give **37**, which in excess acid is ionized to the pentadienyl cation **36b** of inverted planar chirality.

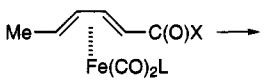
3. Stereoselectivity in C—C Bond-Forming Reactions. One notable feature of the work discussed previously is the wide variation in s-cis/s-trans aldehyde and ketone conformer ratios as a function of the 5-substituent and metal-centered ligand. Such variation should inevitably affect the stereoselectivity of nucleophilic C—C bond-forming reactions at the α-carbonyl function.[1] Though there has been one suggestion to the contrary,[4a] it has generally been assumed that the nucleophile reacts only on the face opposite to the bulky

Fe(CO)$_3$ moiety. Thus, nucleophile addition to the s-cis conformer leads to the derivative termed ψ-exo, while the s-trans conformer gives the ψ-endo product.[22]

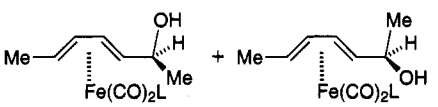


We present here results on the reactions of the sorbaldehyde series **2**, **3**, and **5a** with MeMgI and MeLi; the characteristic of this series is a decreasing s-cis/s-trans ratio in the order **2** (ca. 3.0)[14] > **3** (ca. 0.5) > **5a** (ca. 0.05).

Reaction of the tricarbonyl **2** with MeMgI at −78 °C gave a 1:2.5 mixture of the ψ-exo and ψ-endo alcohols **38** and **39**.[23,24] A reaction with MeLi under the same conditions gave the same mixture in a ratio of 1:1.2.



2, 3, 23, 5a, 16a



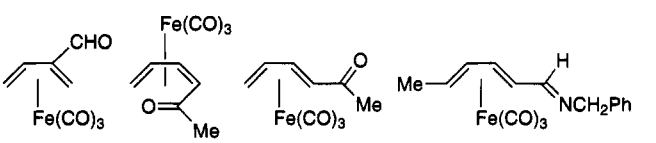
38, 40, 42a (Ψ-exo) **39, 41, 43a** (Ψ-endo)

		reagent			
2	L = CO, X = H	MeMgI	**38**	1:2.5	**39**
		MeLi		1:1.2	
3	L = PPh_3, X = H	MeMgI	**40**	1.9:1	**41**
		MeLi		3.2:1	
23	L = PPh_3, X = Me	$NaBH_4$		0:1	
5a	L = PPh_2(neoMen), X = H	MeMgI	**42a**	1:0	**43a**
16a	L = PPh_2(neoMen), X = Me	$LiAlH_4$		1:2	

In contrast, reaction of the PPh_3-substituted complex **3** with MeMgI and MeLi gave a mixture of **40** and **41** in ratios of 1.9:1 and 3.2:1, respectively. The reversed stereoselectivity was confirmed by the $NaBH_4$ reduction of **23** to give exclusively **41**. In the case of the tricarbonyl analogue of **23**[25] it has been suggested that this high diastereoselectivity arises from delivery of hydride from the face opposite the iron to the ketone exclusively in the s-cis conformation. The s-cis conformation of **23** has been confirmed by a single-crystal structure determination (Figure 1, Table 1). Though the ketonic moiety is twisted out of the diene plane, the s-cis geometry is clearly apparent.

Complex **5a**, which is almost entirely s-trans in solution, yields only a *single* product on reaction with MeMgI, which is formulated as the ψ-exo alcohol **42a**. One may note that, in contrast to **3**, the ketone diastereoisomer **16a** of the same planar chirality as **5a** exhibits a significant concentration of the s-trans conformer in solution. Surprisingly, **16a** is inert to $NaBH_4$ but is reduced by $LiAlH_4$ in lower yield to give a 1:2 mixture of **42a** and **43a**.

Diastereoselectivity in nucleophile addition to α-carbonyl functionalities is clearly dependent upon both nucleophile (and the nature of the countercation) and on substrate structure. Thus, the diastereoselectivity of nucleophile addition to **44** is reversed when MeLi is replaced by $LiMe_2Cu$.[4a] The cis- and trans-ketone complexes **45** and **46** yield only single diastereoisomers on reaction with alkyllithium reagents,[26,27] while transformation of (sorbaldehyde)Fe(CO)$_3$ to the imine **47** promotes a much higher diastereoselectivity in reactions with organometallic nucleophiles.[28]



44 **45** **46** **47**

For the reactions of **2**, **3**, and **5a** with MeMgI and MeLi, the increasing proportion of ψ-exo complex formed with increasing population of the s-trans conformer is not consistent with simple exo addition of nucleophile. Either the s-cis/s-trans ratio is altered by adduct formation prior to rate-determining C—C bond formation or nucleophile addition occurs at the endo face of the complex, possibly through initial addition at CO followed by transfer to the aldehydic carbon. For reactions with MeMgI, the ψ-exo/ψ-endo ratio mirrors closely the s-cis/s-trans ratio, though the reactions of **2** and **3** with MeLi mirror less clearly the s-cis/s-trans ratio, indicating perhaps some kinetic selectivity in nucleophile addition between s-cis and s-trans conformations. The structures of **48** and **49**, isolated from reaction of (butadiene)Fe(CO)$_3$ with ArLi followed by ethylation,[29] clearly indicate attack at M—CO, and kinetic measurements[30] using Fe(CO)$_4$L complexes (L = CO, PPh_3, $P(OMe)_3$) show that rates of such reactions at Fe—CO groups are comparable with even some of the fastest reactions of Grignard reagents with free aldehydes.[31] Recently, it has been shown that reaction of (butadiene)-Fe(CO)$_3$ with hydridic reagents such as KEt_3BH and

(22) ψ-exo and ψ-endo designations are based on the predicted lowest energy conformation of the OH group relative to the diene plane. Generally, the R_f values are in the order ψ-exo < ψ-endo: (a) Kuhn, D. E.; Lillya, C. P. *J. Am. Chem. Soc.* **1970**, *92*, 3065. (b) Kuhn, D. E.; Lillya, C. P. *J. Am. Chem. Soc.* **1972**, *94*, 1682. (c) Grée, R.; Laabasi, M.; Mosset, P.; Carrié, R. *Tetrahedron Lett.* **1984**, *25*, 6393.

(23) Ratios are based on NMR analysis of the crude reaction mixture before separation, since endo → exo rearrangement has been reported on chromatography: Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 3955. An exo:endo ratio of 53:47 has been quoted for this reaction: Heitz, M. P. Doctorat ès Sciences Physiques Thesis, Universiy of Strasbourg, Strasbourg, France, 1983.

(24) The stereochemistry of the ψ-exo isomer has been established by X-ray crystallography: Riley, P. E.; Davis, R. E. *Acta Crystallogr.* **1976**, *32B*, 381.

(25) Clinton, N. A.; Lillya, C. P. *J. Am. Chem. Soc.* **1970**, *92*, 3058.

(26) Takemoto, Y.; Takeuchi, J.; Iwata, C. *Tetrahedron Lett.* **1993**, *34*, 6067.

(27) Franck-Neumann, M.; Chemla, P.; Martina, D. *Synlett* **1990**, 641.

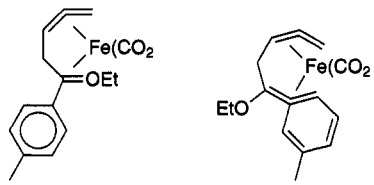
(28) Takemoto, Y.; Takeuchi, J.; Iwata, C. *Tetrahedron Lett.* **1993**, *34*, 6069.

(29) Jiabi, C.; Guixin, L.; Weihua, X.; Xianglin, J.; Meicheng, S.; Youqi, T. *J. Organomet. Chem.* **1985**, *286*, 55.

(30) Darensbourg, M. Y.; Conder, H. L.; Darensbourg, D. J.; Hasday, C. *J. Am. Chem. Soc.* **1973**, *95*, 5919.

(31) Holm, T. *Acta Chim. Scand.* **1969**, *23*, 579.

$LiAlH_4$ to give [(*anti*-methallyl)$Fe(CO)_3$]$^-$ proceeds via initial formation of a metal formyl intermediate.[32]



48 49

C. Experimental Section

All reactions involving iron complexes were carried out in dry, degassed solvents under nitrogen. The ligands (+)-PPh_2(neoMen),[33] (−)-PPh_2(Men),[34] and (−)-PPh_2(OMen)[35] were prepared by literature procedures; (+)-P(*o*-anisyl)PhMe was the kind gift of Professor S. Juge (Université de Cergy-Pontoisse). The dienes 5-phenyl-2,4-pentadienal,[36] methyl 2,4-pentadienoate,[37] methyl 5-formyl-2,4-pentadienoate,[38] 5-methoxy-2,4-pentadienal,[11] 5-(benzoyloxy)-2,4-pentadienal,[39] and 3,5-heptadien-2-one[40] were prepared by literature methods. NMR spectra were recorded on a JEOL GSX 270 spectrometer; temperatures were measured using the built-in copper/constantan thermocouple. Line-shape analyses were performed using the EXCHANGE program (R. E. D. McClung, Univesity of Alberta). ^1H and ^{13}C chemical shifts are measured in ppm relative to tetramethylsilane; ^{31}P chemical shifts are measured in ppm relative to 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer. Preparative thin-layer chromatography was performed on a Harrison Research 7924 chromatotron using 2 mm silica gel (type $PF60_{254}$) plates.

1. Preparation of (5-phenyl-2,4-pentadienal)$Fe(CO)_3$. 5-Phenyl-2,4-pentadienal (3.5 g, 22 mmol) and $Fe_2(CO)_9$ (16 g, 44 mmol) were sonolyzed overnight in toluene (50 mL). Diethyl ether (40 mL) was added, and the mixture was filtered through Celite and the solvent evaporated. Purification by column chromatography (grade IV alumina, 1/9 ethyl acetate/40−60 °C petroleum ether) gave the product as a yellow solid (4.6 g, 73%). Mp: 159−161 °C. Anal. Calcd (found): C, 56.4 (56.5); H, 3.36 (3.32). Infrared (hexane): 2063, 2003, 1987 cm^{-1}. ^1H NMR (C_6D_6): 9.06 (H1, d, J_{12} = 3.4 Hz), 0.93 (H2, dd), 5.27 (H3, m), 5.02 (H4, m), 1.99 (H5, d), 6.9−7.1 (Ph, m).

Other (diene)$Fe(CO)_3$ complexes were prepared in the same way.

(2,4-hexadienal)$Fe(CO)_3$: red oil; infrared (hexane) 2059, 1999, 1983 cm^{-1}; ^1H NMR (C_6D_6) 9.00 (H1, d, J_{12} = 3.7 Hz), 0.66 (H2, dd), 5.08 (H3, m), 4.26 (H4, m), 0.83 (H5, m), 0.88 (Me, d).

(5-methoxy-2,4-pentadienal)$Fe(CO)_3$: yellow solid; infrared (hexane) 2059, 2002, 1987 cm^{-1}; ^1H NMR (C_6D_6) 8.90 (H1, d, J_{12} = 4.1 Hz), 0.31 (H2, dd), 4.90 (H3, dd), 4.60 (H4, t), 2.87 (H5, d), 2.82 (Me, s).

(5-(benzoyloxy)-2,4-pentadienal)$Fe(CO)_3$: yellow solid; infrared (hexane) 2068, 1998 cm^{-1}; ^1H NMR (C_6D_6) 8.90 (H1, d, J_{12} = 2.5 Hz), 0.35 (H2, dd), 5.11 (H3, dd), 4.59 (H4, t), 4.06 (H5, d), 6.8−7.2 (Ph, m).

(methyl 2,4-pentadienoate)$Fe(CO)_3$: red oil; infrared (hexane) 2067, 2007, 1995 cm^{-1}; ^1H NMR (C_6D_6) 0.80 (H2, d), 5.57 (H3, m), 4.41 (H4, m), −0.06 ($H5_{inner}$, dd), 1.23 ($H5_{outer}$, dd), 3.29 (Me, s).

(methyl 2,4-hexadienoate)$Fe(CO)_3$: orange oil; infrared (hexane) 2059, 2003, 1987 cm^{-1}; ^1H NMR (C_6D_6) 0.81 (H2, d), 5.45 (H3, m), 4.28 (H4, m), 0.71 (H5, m), 0.88 (Me, d), 3.32 (CO_2Me, s).

(3,5-heptadien-2-one)$Fe(CO)_3$: yellow oil; infrared (hexane) 2059, 2001, 1995 cm^{-1}; ^1H NMR (C_6D_6) 0.68 (H2, d), 5.49 (H3, dd), 4.29 (H4, dd), 0.78 (H5, m), 1.72 (COMe, s), 0.93 (Me, d).

(methyl 5-formyl-2,4-pentadienoate)$Fe(CO)_3$: yellow solid; infrared (hexane) 2079, 2019 cm^{-1}; ^1H NMR (C_6D_6) 8.89 (H1, d, J_{12} = 2.9 Hz), 0.66 (H2, dd), 5.09 (H3, m), 5.38 (H4, m), 0.96 (H5, m), 3.25 (CO_2Me).

(2-methyl-1,3-butadiene)$Fe(CO)_3$: yellow oil; infrared (hexane) 2043, 1981, 1973 cm^{-1}; ^1H NMR (C_6D_6) 0.30 ($H1_{inner}$, dd), 1.80 ($H1_{outer}$, t), 5.26 (H3, t), 0.00 ($H4_{inner}$, dd), 1.63 $H4_{outer}$, dd), 2.15 (Me, s).

2. Preparation of (2,4-pentadienal)$Fe(CO)_3$. (methyl 2,4-pentadienoate)$Fe(CO)_3$ (2.0 g, 7.9 mmol) was stirred in THF (30 mL) at −78 °C; diisobutylaluminum hydride (DIBAL; 16 mmol, 1 M solution in toluene) was added by syringe and the mixture warmed to room temperature. Water (50 mL) was added and the product extracted with diethyl ether (3 × 50 mL), dried over $MgSO_4$, and evaporated to give (2,4-pentadienol)$Fe(CO)_3$ (1.7 g, 96%). The alcohol was stirred in CH_2Cl_2 (40 mL) with activated 3 Å molecular sieves at −15 °C. Acetic acid (0.8 mL) and pyridinium dichromate (2.85 g, 7.5 mmol) were added and the reaction monitored to completion by TLC. The mixture was filtered, evaporated, and chromatographed (grade IV alumina, 1/4 ethyl acetate/40−60 °C petroleum ether) to give (2,4-pentadienal)$Fe(CO)_3$ as a red oil (0.7 g, 41%): infrared (hexane) 2047, 1983, 1975 cm^{-1}; ^1H NMR (C_6D_6) 8.95 (H1, d, J_{12} = 3.4 Hz), 0.62 (H2, dd), 5.22 (H3, m), 4.43 (H4, m), 0.02 ($H5_{inner}$, qd), 1.23 ($H5_{outer}$, qd).

Coupling constants for the tricarbonyls are in the range $J_{2-3} \approx J_{4-5_{inner}} \approx 9-10$ Hz, $J_{3-4} \approx 4.5-7.0$ Hz, $J_{5-Me} \approx 6.0-6.3$ Hz, and $J_{5_{inner}-5_{outer}} \approx 2.7-3.5$ Hz, except for the methoxy and benzoyloxy complexes, where $J_{4-5_{inner}} \approx 6.0-6.5$ Hz.

3. Preparation of (methyl 2,4-pentadienoate)$Fe(CO)_2PPh_3$ (18). (methyl 1,3-pentadienoate)$Fe(CO)_3$ (1.0 g, 4 mmol) and PPh_3 (1.2 g, 6 mmol) were dissolved in acetone (40 mL); $Me_3NO{\cdot}2H_2O$ (1.0 g, 9 mmol) was added and the mixture stirred at 40 °C until infrared sampling indicated completion. Diethyl ether (50 mL) was added to the cooled solution, which was filtered through Celite and evaporated. Column chromatography (grade IV alumina, 1/9 ethyl acetate/40−60 °C petroleum ether) gave **18** as a yellow solid (0.89 g, 46%), which was recrystallized from ethyl acetate/60−80 °C petroleum ether. Mp: 49−52 °C. Anal. C, 64.2 (64.6); H, 4.73 (4.69). Infrared (hexane): 1999, 1947 cm^{-1}. ^1H NMR (C_6D_6, 50 °C): 0.70 (H2, br), 5.98 (H3, dd), 4.58 (H4, m), −0.13 ($H5_{inner}$, br), 1.21 ($H5_{outer}$, br), 3.42 (Me, s), 6.8−7.5 (PPh_3, m). ^{13}C NMR (CD_2Cl_2, −70 °C): 38.8, 45.0 (C2, C5), 82.8, 84.8 (C3, C4), 51.0, 173.9 (CO_2Me), 212.7 (28.2) (CO_{basal}), 220.1 (9.4) (CO_{axial}), 127.7 (9.4), 129.7, 132.4 (10.8), 134.9 (39.4) (PPh_3). ^{31}P (CD_2Cl_2, 20 °C): 72.5 (br). Other PPh_3 complexes exhibit similar ^{13}C and ^1H ligand subspectra. Values in brackets represent J_{P-C}.

Other phosphine-substituted complexes were prepared in the same way.

19: yield 45%; mp 102−105 °C. Anal. Calcd (found): C, 65.8 (66.2); H, 4.61 (4.89). Infrared (hexane): 1999, 1943, 1931 cm^{-1}; ^1H NMR (C_6D_6, 60 °C): 9.34 (H1, d), 0.66 (H2, br), 5.60 (H3, dd), 4.62 (H4, m), 0.08 ($H5_{inner}$, t), 1.39 ($H5_{outer}$, br); ^{13}C NMR (CD_2Cl_2, −60 °C): 46.3, 50.1 (C2, C5), 82.3, 87.2 (C3, C4), 198.1 (C1), 212.8 (29.8) (CO_{basal}), 219.6 (9.8) (CO_{axial}). ^{31}P NMR (CD_2Cl_2, 20 °C): 72.3 (br).

20: yield 56%; mp 131−134 °C. Anal. Calcd (found): C, 66.7 (66.8); H, 4.34 (4.22). Infrared (hexane): 1991, 2005 (sh), 1945 cm^{-1}. ^1H NMR (C_6D_6, 20 °C): 8.91 (H1, d), 0.09 (H2,

(32) Chang, S.; White, P. S.; Brookhart, M. *Organometallics* **1993**, *12*, 3636.
(33) Morrison, J. D.; Masler, W. F. *J. Org. Chem.* **1974**, *39*, 270.
(34) Tanaka, M.; Ogata, I. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1094.
(35) Coller, K. S.; Lewis, E. S. *J. Org. Chem.* **1978**, *43*, 571.
(36) Meyers, A. I.; Nabeya, A.; Adickes, H. W.; Politzer, I. R.; Malone, G. R.; Kovelsky, A. C.; Nolen, R. L.; Portnay, R. C. *J. Org. Chem.* **1973**, *38*, 36.
(37) Muskat, I. E.; Brunner, C.; Lowenstein, J. S. *J. Am. Chem. Soc.* **1930**, *52*, 326.
(38) Grée, R.; Tourbah, H.; Carrié, R. *Tetrahedron Lett.* **1986**, *27*, 4983.
(39) Becker, J. *Synthesis* **1980**, 589.
(40) Attenburrow, J.; Cameron, A. F. B.; Chapman, J. H.; Evans, R. M.; Hems, B. A.; Jansen, A. B. A.; Walker, T. *J. Chem. Soc.* **1952**, 1094.

br), 5.25 (H3, t), 4.92 (H4, br), 4.36 (H5, br), 6.9–8.0 (Ph, m). ^{13}C NMR (CD_2Cl_2, −40 °C): 58.3 (C2), 78.2, 80.4, 86.9 (C3, C4, C5), 197.5 (C1), 164.2 ($PhCO_2$), 128–136 (Ph), 210.0 (5.3), 213.9 (11.5) (CO_{basal}). ^{31}P NMR (CD_2Cl_2, 20 °C): 61.7 (br).

21: yield 74%; mp 36–42 °C. Anal. Calcd (found): C, 64.2 (64.4); H, 4.77 (5.02). Infrared (hexane): 1997, 1943 cm^{-1}. ^{1}H NMR (C_6D_6, 55 °C): 8.94 (H1, d), 0.23 (H2, br), 4.98 (H3, t), 4.80 (H4, t), 2.51 (H5, br), 2.87 (MeO, s). ^{13}C NMR (CD_2Cl_2, −60 °C): 57.2 (C2, br), 77.7 (C3 or C4; second resonance broadened and not detected), 105.4 (C5), 60.9 (MeO), 197.5 (C1), 211.0, 213.9 (10.3) (CO_{basal}). ^{31}P NMR (CD_2Cl_2, 20 °C): 62.3 (br).

22: yield 71%; mp 86–88 °C. Anal. Calcd (found): C, 59.4 (59.6); H, 4.95 (5.13). Infrared (hexane): 1991, 1935 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 9.18 (H1, d), 0.31 (H2, 5, m), 5.28 (H3, t), 4.59 (H4, dd), 1.09 (Me, d), 3.10 (P—OMe, d), 7.0–7.7 (Ph, m). ^{13}C NMR (CD_2Cl_2, −60 °C): 58.3, 60.4 (C2, C5), 82.3, 90.1 (C3, C4), 18.0 (Me), 197.6 (C1), 210.7, 213.0 (12.1) (CO_{basal}). ^{31}P NMR (CD_2Cl_2, 20 °C): 170.7.

23: yield 84%; mp 127–128 °C. Anal. Calcd (found): C, 66.9 (66.9); H, 5.17 (5.21). Infrared (hexane): 1999, 1987 (sh), 1943, 1927 (sh) cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 0.05–0.35 (H2, 5, m), 5.85 (H3, t), 4.65 (H4, dd), 0.99 (Me, d), 1.48 (COMe, s). ^{13}C NMR (CD_2Cl_2, −50 °C): 57.5, 61.9 (C2, C5), 83.6, 89.3 (C3, C4), 18.6 (Me), 30.6, 205.5 (COMe), 212.2 (4.1), 215.3 (9.3) (CO_{basal}). ^{31}P NMR (CD_2Cl_2, 20 °C): 63.2.

24: yield 37%; mp 113–114 °C. Anal. Calcd (found): C, 64.2 (64.5); H, 4.73 (4.69). Infrared (hexane): 1999, 1947 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 9.08 (H1, d), 0.15 (H2, m), 5.20 (H3, m), 5.75 (H4, m), 0.48 (H5, m), 3.18 (CO_2Me, s). ^{13}C NMR (CD_2Cl_2, −60 °C): 49.4, 60.4 (C2, C5), 84.6, 88.1 (C3, C4), 50.7, 172.8 (CO_2Me), 197.2 (C1), 209.7 (8.0), 210.7 (8.0) (CO_{basal}). ^{31}P NMR (CD_2Cl_2, 20 °C): 60.9.

25: yield 33%; mp 158–160 °C. Anal. Calcd (found): C, 64.8 (64.9); H, 5.00 (5.07). Infrared (hexane): 1986, 1924 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 0.09 (H2, t), 5.87 (H3, br), 4.59 (H4, dd), −0.28 (H5, br), 1.05 (Me, d), 3.19 (CO_2Me, s). ^{13}C NMR (CD_2Cl_2, −40 °C): 48.5, 61.8 (C2, C5), 80.6, 83.6 (C3, C4), 18.3 (Me), 50.6, 174.1 (CO_2Me), 211.8 (4.9), 214.7 (8.8) (CO_{basal}). ^{31}P NMR (CD_2Cl_2, 20 °C): 64.9.

3: yield 65%; mp 143–144 °C. Anal. Calcd (found): C, 66.4 (66.2); H, 4.89 (4.96). Infrared (hexane): 1986, 1930 cm^{-1}. ^{1}H (C_6D_6, 20 °C): 9.10 (H1, d), 0.16 (H2, 5, m), 5.31 (H3, t), 4.62 (H4, q), 1.04 (Me, d). ^{13}C (CD_2Cl_2, −60 °C): 59.3, 61.7 (C2, C5), 82.3, 90.4 (C3, C4), 18.1 (Me), 197.5 (C1), 211.7 (4.9), 214.8 (8.8) (CO_{basal}). ^{31}P NMR (CD_2Cl_2, 20 °C): 62.8. A sample of (2*S*)-**3** was obtained by the same procedure from homochiral (+)-(2*S*)-2,4-hexadienal resolved using (−)-ephedrine.[41]

5a,b: yield 39%, separated by Chromatotron (1/9 ethyl acetate/40–60 °C petroleum ether). **5a**: semisolid. Anal. Calcd (found): C, 67.7 (67.5); H, 6.95 (7.21). Infrared (hexane): 1984, 1928 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 9.15 (H1, d), −0.60 (H2, 4, br), 5.13 (H3, br), 4.40 (H4, dd), 1.12 (Me(diene), d), 0.80 (Me(neoMen), d), 1.33, 0.19 (CH*Me*$_2$, dd), 1.2–3.2 (cyclohexyl, *CH*Me$_2$, m). ^{13}C NMR (CD_2Cl_2, −50 °C): 59.5, 64.5 (C2, C5), 84.3, 90.2 (C3, C4), 19.7 (Me), 198.8 (C1), 212.2, 215.8 (10.7) (CO_{basal}), 16.9, 17.9, 19.4 (11.7), 23.1, 28.1 (6.9), 28.5, 28.9, 30.7, 35.6 (17.6), 38.9 (neoMen), 127.4–136.7 (Ph) (other menthyl and neomenthyl complexes exhibit similar ^{1}H and ^{13}C ligand subspectra). ^{31}P NMR (CD_2Cl_2, 25 °C): 65.5 (br). **5b**: semisolid. Anal. Calcd (found): C, 67.7 (67.3); H, 6.95 (7.19). Infrared (hexane): 1978, 1920 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 9.19 (H1, d), 0.10, −0.25 (H2, 5, br), 5.36 (H3, br), 4.48 (H4, dd), 1.10 (Me, d). ^{13}C NMR (CD_2Cl_2, −50 °C): 59.2, 62.9 (C2, C5), 82.4, 90.1 (C3, C4), 19.7 (Me), 198.3 (C1), 212.1, 215.4 (8.0) (CO_{basal}). ^{31}P NMR (CD_2Cl_2, 25 °C): 65.6 (br).

6a,b: yield 31%; separated by Chromatotron (1/9 ethyl acetate/40–60 °C petroleum ether). **6a**: mp 148–149 °C. Anal. Calcd (found): C, 67.7 (68.0); H, 6.95 (7.42). Infrared (hexane): 1987, 1927 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 9.18 (H1, d), 0.32, −0.41 (H2,3, br), 5.30 (H3, br), 4.39 (H4, dd), 0.99 (Me, d). ^{31}P NMR (CD_2Cl_2, 20 °C): 66.8 (br). **6b**: mp 126–127 °C. C, 67.7 (67.7); H, 6.95 (7.23). Infrared (hexane): 1983, 1933, 1927 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 8.99 (H1, br), 0.05, −0.30 (H2,3, br), 5.38 (H3, br), 4.41 (H4, br), 1.00 (Me, d). ^{31}P NMR (CD_2Cl_2, 20 °C): 67.1 (br).

7a,b: yield 61%; separated by Chromatotron (1/9 ethyl acetate/40–60 °C petroleum ether). **7a**: oil; M^+ = 548.1780 (calculated and found). Infrared (hexane): 1989, 1935 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 9.31 (H1, d), 0.31, −0.05 (H2,3, br), 5.38 (H3, t), 4.54 (H4, dd), 0.96 (Me, d). ^{31}P NMR (CD_2Cl_2, 20 °C): 164.0 (br). **7b**: mp 107–108 °C. Anal. Calcd (found): C, 65.7 (65.9); H, 6.75 (6.70). Infrared (hexane): 1989, 1935 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 9.17 (H1, d), 0.15, −0.09 (H2,3, br), 5.33 (H3, t), 4.65 (H4, dd), 0.92 (Me, d). ^{31}P NMR (CD_2Cl_2, 20 °C): 163.3.

8a,b: yield 36%; not separable by chromatography. A 76% enriched sample of the 2*R* diastereoisomer **8b** was prepared from similarly enriched (2*R*)-(2,4-hexadienal)Fe(CO)$_3$ obtained by resolution using (−)-ephedrine.[41] M^+: 438.0670 (calculated and found). Infrared (hexane): 1987, 1931 cm^{-1}. ^{1}H NMR ($C_6D_5CD_3$, 20 °C): 9.14 (H1, d), 0.30, 0.49 H2,5, m), 5.17 (H3, m), 4.51 (H4, m), 0.73 (Me, d), 3.06 (OMe, s), 1.60 (P—Me, d), 6.3–7.5 (Ph, m). ^{31}P NMR (CD_2Cl_2, 20 °C): 36.8. Minor resonances due to **8a** may also be observed.

9a,b: 15% yield, not separable by chromatography. An optically pure sample of the 2*R* diastereoisomer **9b** was prepared from the homochiral 2*R* tricarbonyl obtained by resolution using (−)-ephedrine.[4b] Mp: 168–171 °C. Anal. Calcd (found): C, 64.6 (64.9); H, 6.42 (6.93). Infrared (hexane): 2011, 2001, 1959, 1947 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 8.82 (H1, br), −0.20 (H2, br), 5.30 (H3, t), 5.70 (H4, t), 3.48 (CO_2Me, s), H5 obscured by neomenthyl; ^{31}P NMR (CD_2Cl_2, 20 °C): 61.5 (br).

10a,b: yield 37%; separated by Chromatotron (1/9 ethyl acetate/40–60 °C petroleum ether). **10a**: mp 105–107 °C. Anal. Calcd (found): C, 67.2 (67.1); H, 6.76 (6.83). Infrared (hexane): 1989, 1935, 1931 cm^{-1}. ^{1}H NMR (C_6D_6, 80 °C): 9.16 (H1, d), 5.36 (H3, m), 4.69 (H4, m), −0.73 ($H5_{inner}$, t), H2, $H5_{outer}$ obscured by neomenthyl; ^{13}C NMR (CD_2Cl_2, −40 °C): 48.5, 60.1 (C2, C5), 85.8, 86.8 (C3, C4), 198.0 (C1), 211.7 (5.0), 214.7 (10.7) (CO_{basal}). ^{31}P NMR (CD_2Cl_2, 20 °C): 68.4 (br). **10b**: mp 149–150 °C. Anal. Calcd (found): C, 67.2 (67.3); H, 6.76 (6.79). Infrared (hexane): 1989, 1935, 1931 cm^{-1}. ^{1}H NMR (C_6D_6, 80 °C): 9.15 (H1, d), 5.43 (H3, t), 4.43 (H4, br), −0.07 ($H5_{inner}$, br), H2,$H5_{outer}$ obscured by neomenthyl. ^{13}C NMR (CD_2Cl_2, −40 °C): basal isomer, 48.9, 59.4 (C2, C5), 86.4, 93.5 (C3, C4), 197.4 (C1), 213.2 (25.0) (CO_{basal}), 220.2 (13.0) (CO_{axial}); axial isomer, 49.3, 70.5 (C2, C5), 82.7, 84.2 (C3, C4), 197.8 (C1), 211.5 (5.1), 214.4 (6.3) (CO_{basal}). ^{31}P NMR (CD_2Cl_2, 20 °C): 66.9 (br), 71.7 (br).

11a,b: yield 48%; separated by Chromatotron (1/9 ethyl acetate/40–60 °C petroleum ether). **11a**: mp 148–151 °C. Anal. Calcd (found): C, 70.8 (71.2); H, 6.62 (6.88). Infrared (hexane): 1985, 1925 cm^{-1}. ^{1}H NMR (C_6D_6, 60 °C): 9.30 (H1, d), 0.30 (H2, m), 5.35 (H3, H4, m), H5, Ph obscured by PPh_2(neoMen). ^{13}C NMR (CD_2Cl_2, −40 °C): 58.7, 65.4 (C2, C5), 80.7, 86.5 (C3, C4), 198.5 (C1), 212.0 (4.0), 214.2 (9.4) (CO_{basal}), Ph obscured by PPh_2(neoMen). ^{31}P NMR (CD_2Cl_2, 20 °C): 63.0 (br). **11b**: mp 66–70 °C. Anal. Calcd (found): C, 70.8 (70.8); H, 6.62 (6.96). Infrared (hexane): 1985, 1925 cm^{-1}. ^{1}H NMR (C_6D_6, 60 °C): 9.02 (H1, d), 0.06 (H2, br), 5.43 (H3, t), 5.35 (H4, dd), H5, Ph obscured by PPh_2(neoMen). ^{13}C NMR (CD_2Cl_2, −40 °C): 59.6, 64.1 (C2, C5), 79.6, 88.1 (C3, C4), 198.3 (C1), 211.9 (5.4), 214.1 (8.8) (CO_{basal}), Ph obscured by PPh_2(neoMen). ^{31}P NMR (CD_2Cl_2, 20 °C): 61.3.

12a,b: yield 54%; separated by Chromatotron (1/9 ethyl acetate/40–60 °C petroleum ether). **12a**: mp 98–103 °C. Anal. Calcd (found): C, 67.7 (67.5); H, 6.11 (6.11). Infrared (hexane): 1997, 1943 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 9.06 (H1, d), 0.07 (H2, dd), 5.09 (H3, t), 4.78 (H4, t), 3.32 (H5, dd), Ph obscured by PPh_2(neoMen). ^{31}P NMR (CD_2Cl_2, 20 °C): 64.8

(41) Howell, J. A. S.; Palin, M. G. Unpublished results.

Table 5. Crystallographic Data[a]

	14a	15b	17a	23
empirical formula	$C_{62}H_{78}Fe_2O_8P_2$	$C_{30}H_{37}FeO_4P$	$C_{29}H_{37}Fe_2O_2P$	$C_{54}H_{50}Fe_2O_6P_2$
fw	1124.88	548.42	504.41	968.58
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	triclinic
space group	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P\bar{1}$
unit cell dimens	a = 9.860(4) Å, b = 35.815(9) Å, c = 16.519(4) Å	a = 8.7353(9) Å, b = 18.055(3) Å, c = 9.9894(11) Å, β = 113.395(8)	a = 10.151 (3) Å, b = 14.780(3) Å, c = 17.804(4) Å	a = 12.081(2) Å, b = 13.914(2) Å, c = 16.835(2) Å, γ = 113.18(2)°, α = 93.33(2)°, β = 109.47(2)°, γ = 113.18(2)°
V (Å^3)	5834(3)	1446.0(3)	2671.2(11)	2393.5(6)
Z	4	2	4	4
density (calcd) (Mg/m^3)	1.281	1.260	1.254	1.344
abs coeff (mm^{-1})	0.605	0.608	0.647	0.723
F(000)	2384	580	1072	1008
cryst size (mm)	0.40 × 0.33 × 0.38	0.38 × 0.41 × 0.25	0.34 × 0.45 × 0.48	0.43 × 0.51 × 0.40
θ range for data collecn (deg)	2.10–23.99	2.22–29.96	2.29–21.99	2.10–31.95
index ranges	$0 \le h \le 10, 0 \le k \le 36, -16 \le l \le 16$	$0 \le h \le 12, 0 \le k \le 25, -14 \le l \le 12$	$0 \le h \le 10, 0 \le k \le 15, 0 \le l \le 18$	$-17 \le h \le 15, -19 \le k \le 20, 0 \le l \le 25$
no. of rflns collected	9490	4732	1583	11 757
no. of indep rflns	8706 (R(int) = 0.0255)	4328 (R(int) = 0.0180)	1583	9425 (R(int) = 0.0000)
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/no. of params	8706/0/669	4328/1/335	1583/0/302	9425/0/579
goodness of fit on F^2	0.718	0.774	1.082	1.037
final R indices ($I > 2\sigma(I)$)	R_1 = 0.0431, wR_2 = 0.1250	R_1 = 0.0380, wR_2 = 0.1012	R_1 = 0.0481, wR_2 = 0.1086	R_1 = 0.0788, wR_2 = 0.2201
R indices (all data)	R_1 = 0.1195, wR_2 = 0.1813	R_1 = 0.0818, wR_2 = 0.1234	R_1 = 0.0613, wR_2 = 0.1171	R_1 = 0.0813, wR_2 = 0.2413
abs structure param	−0.03(3)	−0.01(2)	−0.01(6)	
largest diff peak and hole (e/Å^3)	0.223 and −0.225	0.386 and −0.204	0.217 and −0.332	0.589 and −1.872

[a] $R_1 = [\sum||F_o| - |F_c||]/\sum|F_o|$ (based on F); w$R_2 = [[\sum_w(|F_o - F_c|)^2]/[\sum w(|F_o|^2]]^{1/2}$ (based on F^2). $w = q/[(\sigma F_o)^2 + (aP)^2 + bP + d + e \sin\theta]$. Goodness of fit $= [\sum w(|F_o^2| - |F_c^2|)^2/(N_{obs} - N_{params})]^{1/2}$.

(br). **12b**: mp 81–82 °C. Anal. Calcd (found): C, 67.7 (67.7); H, 6.11 (6.24). Infrared (hexane): 2001, 1993 (sh), 1947 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 8.60 (H1, br), −0.25 (H2, br), 5.30 (H3, t), 4.92 (H4, t), 4.30 (H5, dd), Ph obscured by PPh_2(neoMen). ^{31}P NMR (CD_2Cl_2, 20 °C): 64.8 (br).

13a,b: yield 61%; separated by Chromatotron (1/9 ethyl acetate/40–60 °C petroleum ether). **13a**: mp 116–118 °C. Anal. Calcd (found): C, 65.7 (65.8); H, 6.75 (6.87). Infrared (hexane): 2001, 1938 cm^{-1}. ^{1}H NMR (C_6D_6, 55 °C): 9.04 (H1, d), 0.04 (H2, br), 4.89 (H3, br), 4.60 (H4, t), 2.32 (H5, br), 2.71 (MeO, s). ^{31}P NMR (CD_2Cl_2, 20 °C): 65.4 (br). **13b**: mp 49–54 °C. Anal. Calcd (found): C, 65.7 (65.6); H, 6.75 (7.18). Infrared (hexane): 2001, 1985, 1932 cm^{-1}. ^{1}H NMR (C_6D_6, 55 °C): 9.16 (H1, br), 0.10 (H2, br), 5.01 (H3, br), 4.57 (H4, br), 2.35 (H5, br), 3.00 (MeO, s). ^{31}P NMR (CD_2Cl_2, 20 °C): 64.9 (br).

14a,b: yield 19%; separated by Chromatotron (1/9 ethyl acetate/40–60 °C petroleum ether). **14a**: mp 153–155 °C. Anal. Calcd (found): C, 66.2 (66.5); H, 6.94 (7.20). Infrared (hexane): 1986, 1930 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 0.00 (H2, t), 5.82 (H3, m), 4.46 (H4, dd), −0.85 (H5, m), 1.07 (Me, d), 3.50 (CO_2Me, s). ^{13}C NMR (CD_2Cl_2, −65 °C): 46.2, 62.7 (C2, C5), 83.8, 87.5 (C3, C4), 17.2 (Me), 50.9, 174.3 (CO_2Me), 211.8 (3.9), 215.5 (9.8) (CO_{basal}). ^{31}P NMR (CD_2Cl_2, 20 °C): 68.2 (br). **14b**: mp 151–152 °C. Anal. Calcd (found): C, 66.2 (66.5); H, 6.94 (6.88). Infrared (hexane): 1986, 1930 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): −0.10 (H2, t), 5.95 (H3, br), 4.47 (H4, br), −0.79 (H5, dd), 1.04 (Me, d), 3.23 (CO_2Me, s). ^{13}C NMR (CD_2Cl_2, −65 °C): 48.5, 62.2, (C2, C5), 83.7, 87.2 (C3, C4), 17.5 (Me), 50.2, 173.8 (CO_2Me), 212.0 (3.9), 215.2 (9.8) (CO_{basal}). ^{31}P NMR (CD_2Cl_2, 20 °C): 68.0.

15a,b: yield 37%; separated by Chromatotron (1/9 ethyl acetate/40–60 °C petroleum ether). **15a**: mp 49–52 °C. M$^+$: 548.1779 (calculated and found). Infrared (hexane): 1991, 1935 cm^{-1}. ^{1}H NMR (C_6D_6, 60 °C): 0.20 (H2, t), 5.85 (H3, m), 4.62 (H4, m), −1.03 ($H5_{inner}$, br), 3.49 (CO_2Me, s), $H5_{outer}$ obscured by neomenthyl. ^{31}P NMR (CD_2Cl_2, 20 °C): 69.5 (br). **15b**: mp 145–146 °C; Anal. Calcd (found): C, 65.7 (65.8); H, 6.75 (6.78). Infrared (hexane): 1991, 1935 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 0.05 (H2, br), 5.90 (H3, br), 4.68 (H4, br), −1.28 ($H5_{inner}$, br), 3.30 (Me, s, br), $H5_{outer}$ obscured by neomenthyl. ^{31}P NMR (CD_2Cl_2, 20 °C): 69.7, 71.5 (br).

16a,b: yield 76%; separated by Chromatotron (1/9 ethyl acetate/40–60 °C petroleum ether). **16a**: mp 132–135 °C. Anal. Calcd (found): C, 68.1 (68.4); H, 7.14 (7.32). Infrared (hexane): 1991, 1981, 1927 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 0.35 (H2, br), 5.29 (H3, br), 4.41 (H4, dd), −0.70 (H5, dd), 1.00 (Me, br), 1.99 (COMe, br). ^{31}P NMR (CD_2Cl_2, 20 °C): 65.1 (br). **16b**: mp 147–150 °C. Anal. Calcd (found): C, 68.1 (68.1); H, 7.14 (7.35). Infrared (hexane): 1989, 1979, 1927 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 0.09 (H2, t), 5.82 (H3, br), 4.46 (H4, dd), 1.07 (Me, d), 1.89 (COMe, br). ^{31}P NMR (CD_2Cl_2, 20 °C): 67.2 (br).

17a,b: yield 54%. The crude product (4.35 g) was dissolved in 40–60 °C petroleum ether (30 mL) and cooled to 0 °C for 24 h. Filtration provided 0.36 g (16% yield) of pure diastereoisomer **17a** of 2*R* absolute configuration. Mp: 146–148 °C. Anal. Calcd (found): C, 69.1 (69.1); H, 7.34 (7.40). Infrared (hexane): 1972, 1914 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): −0.92 ($H1_{inner}$, $H4_{inner}$, m), 4.61 (H3, t), 1.81 (Me, s), $H1_{outer}$, $H4_{outer}$ obscured by neomenthyl. ^{31}P NMR (CD_2Cl_2, 20 °C): 72.5.

4. Preparation of (sorbaldehyde)Fe(CO)$_2$P(OMe)$_3$ (4). Complex **2** (1.0 g, 4.3 mmol) and P(OMe)$_3$ (0.6 g, 4.8 mmol) were dissolved in toluene (240 mL) and irradiated for 15 h using a 90 W medium-pressure mercury lamp. After filtration and evaporation, the crude product was purified by Chromatotron (1/1 ethyl acetate/40–60 °C petroleum ether) to give the product (400 mg, 50%). Mp: 55–57 °C. Anal. Calcd (found): C, 39.8 (39.7); H, 5.12 (5.48). Infrared (hexane): 1999, 1935 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 9.20 (H1, d), 0.95 (H2, m), 5.17 (H3, m), 4.58 (H4, m), 1.04 (H5, m), 1.27 (Me, d), 3.26 (P–OMe, d). ^{13}C NMR (CD_2Cl_2, −55 °C): 54.9, 57.6 (C2, C5), 80.3, 88.5 (C3, C4), 17.8 (Me), 197.5 (C1), 210.5, 212.8 (16.8) (CO_{basal}). ^{31}P NMR (CD_2Cl_2, 20 °C): 182.6. A sample of (2*S*)-**4** was obtained from (+)-(2*S*)-(2,4-hexadienal)Fe(CO)$_3$ resolved using (−)-ephedrine.[41]

Proton resonances of phosphine and phosphite complexes (particularly those due to terminal diene protons) are broad at room temperature due to exchange processes. Where measurable, coupling constants are similar to those for the

Table 6. Atomic Coordinates ($\times 10^4$) for 14a and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3)[a]

	x	y	z	U(eq)
Fe(1)	1357(1)	9576(1)	9002(1)	40(1)
P(1)	1863(2)	9388(1)	7730(1)	36(1)
O(1)	3695(7)	9300(2)	9882(4)	71(2)
O(2)	−62(7)	8937(2)	9704(4)	79(2)
O(3)	−2217(6)	9538(2)	9078(4)	79(2)
O(4)	−2292(7)	9806(2)	7851(4)	73(2)
C(1)	2781(9)	9408(2)	9523(5)	45(2)
C(2)	446(9)	9186(3)	9390(5)	48(2)
C(3)	3722(11)	10210(3)	9036(6)	73(3)
C(4)	2252(10)	10127(2)	8939(6)	57(2)
C(5)	1394(12)	10082(2)	9607(5)	60(3)
C(6)	61(11)	9949(2)	9487(6)	58(3)
C(7)	−370(10)	9909(3)	8669(5)	54(2)
C(8)	−1691(11)	9754(3)	8472(7)	69(3)
C(9)	−3503(11)	9373(4)	8926(9)	122(6)
C(10)	2746(8)	9756(2)	7181(4)	41(2)
C(11)	4138(8)	9781(3)	7146(5)	50(2)
C(12)	4839(10)	10077(3)	6838(6)	60(3)
C(13)	4113(11)	10373(3)	6541(6)	62(3)
C(14)	2730(11)	10370(2)	6558(5)	60(3)
C(15)	2031(9)	10062(2)	6861(4)	44(2)
C(16)	3039(8)	8995(2)	7605(5)	47(2)
C(17)	3328(8)	8752(2)	8237(6)	49(2)
C(18)	4212(10)	8462(3)	8141(7)	66(3)
C(19)	4813(10)	8395(3)	7401(8)	73(3)
C(20)	4524(10)	8621(3)	6775(7)	71(3)
C(21)	3641(9)	8928(2)	6857(5)	49(2)
C(22)	372(8)	9280(2)	7089(5)	43(2)
C(23)	−631(9)	8987(2)	7452(6)	53(2)
C(24)	−1908(9)	8963(3)	6922(6)	71(3)
C(25)	−1627(11)	8934(3)	6013(7)	87(4)
C(26)	−701(9)	9238(3)	5700(6)	65(3)
C(27)	618(9)	9231(3)	6185(5)	55(2)
C(28)	−1397(11)	9616(3)	5678(6)	83(3)
C(29)	−55(10)	8606(3)	7718(7)	68(3)
C(30)	−1086(12)	8380(3)	8214(9)	102(4)
C(31)	535(12)	8352(3)	7036(8)	98(4)
Fe(2)	8873(1)	6289(1)	6592(1)	41(1)
P(2)	9336(2)	6827(1)	7235(1)	39(1)
O(5)	10072(7)	5720(2)	7650(4)	64(2)
O(6)	6236(7)	6127(2)	7280(5)	87(2)
O(7)	12855(6)	6464(2)	5991(4)	69(2)
O(8)	12049(6)	5893(2)	6239(4)	63(2)
C(32)	9644(8)	5958(2)	7233(6)	45(2)
C(33)	7284(10)	6195(2)	7035(6)	57(2)
C(34)	6348(10)	6623(3)	5518(7)	77(3)
C(35)	7814(10)	6517(3)	5529(5)	61(3)
C(36)	8237(10)	6146(2)	5433(6)	57(3)
C(37)	9585(9)	6048(2)	5562(5)	49(2)
C(38)	10541(9)	6335(2)	5762(5)	46(2)
C(39)	11910(9)	6248(3)	5996(6)	53(2)
C(40)	13327(9)	5776(3)	6585(7)	78(3)
C(41)	8927(8)	7224(2)	6585(5)	42(2)
C(42)	7668(9)	7395(2)	6585(6)	53(2)
C(43)	7348(10)	7668(2)	6040(7)	65(3)
C(44)	8242(13)	7782(3)	5474(7)	71(3)
C(45)	9469(13)	7612(3)	5423(6)	69(3)
C(46)	9819(9)	7341(2)	5983(6)	50(2)
C(47)	8413(8)	6935(2)	8167(5)	50(2)
C(48)	8276(10)	7300(3)	8449(6)	62(3)
C(49)	7617(14)	7372(3)	9168(7)	94(4)
C(50)	7106(14)	7088(4)	9621(7)	104(4)
C(51)	7186(14)	6747(4)	9365(7)	92(4)
C(52)	7820(10)	6658(3)	8639(6)	60(3)
C(53)	11151(9)	6915(2)	7483(5)	47(2)
C(54)	11920(9)	6612(3)	7963(6)	58(2)
C(55)	13426(9)	6718(3)	7976(8)	82(3)
C(56)	13724(11)	7105(3)	8269(9)	102(4)
C(57)	12943(11)	7403(3)	7808(9)	88(4)
C(58)	11425(9)	7317(3)	7808(7)	67(3)
C(59)	13476(12)	7448(3)	6936(9)	101(4)
C(60)	11322(13)	6455(3)	8755(5)	77(3)
C(61)	11211(18)	6719(5)	9461(7)	134(6)
C(62)	12033(14)	6083(4)	8998(9)	124(5)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 7. Atomic Coordinates ($\times 10^4$) for 15b and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3)[a]

	x	y	z	U(eq)
Fe(1)	2068(1)	2911(1)	5647(1)	56(1)
P(1)	−261(1)	2917(1)	6079(1)	46(1)
O(1)	4756(4)	3275(2)	8443(4)	81(1)
O(2)	1887(6)	4421(3)	4577(5)	106(1)
O(3)	4173(5)	1376(3)	8103(5)	92(1)
O(4)	1720(5)	801(2)	7111(4)	79(1)
C(1)	2214(5)	1731(3)	5761(5)	66(1)
C(2)	3343(6)	2057(4)	5232(6)	81(2)
C(3)	2697(7)	2521(4)	4006(6)	90(2)
C(4)	964(8)	2644(4)	3426(5)	86(2)
C(5)	2841(6)	1306(3)	7103(6)	68(1)
C(6)	2196(10)	335(4)	8371(8)	106(2)
C(7)	3675(5)	3112(2)	7372(4)	60(1)
C(8)	1980(6)	3842(4)	5052(5)	74(1)
C(9)	−1942(5)	2467(3)	4554(4)	56(1)
C(10)	−2142(5)	1695(3)	4560(5)	64(1)
C(11)	−3212(6)	1328(4)	3313(6)	84(2)
C(12)	−4072(7)	1719(4)	2050(6)	94(2)
C(13)	−3928(7)	2461(4)	2043(6)	92(2)
C(14)	−2852(6)	2854(4)	3285(4)	74(1)
C(15)	−290(4)	2418(2)	7668(4)	46(1)
C(16)	1182(5)	2267(2)	8868(4)	50(1)
C(17)	1123(6)	1945(2)	10102(4)	61(1)
C(18)	−379(7)	1746(3)	10146(5)	69(1)
C(19)	−1829(6)	1877(3)	8955(5)	66(1)
C(20)	−1797(5)	2209(2)	7722(4)	59(1)
C(21)	−1127(5)	3849(2)	6173(4)	52(1)
C(22)	143(6)	4409(2)	7203(5)	61(1)
C(23)	−726(8)	5165(3)	6950(7)	83(1)
C(24)	−2405(8)	5186(3)	7063(7)	92(2)
C(25)	−3627(7)	4607(3)	6073(6)	81(1)
C(26)	−2816(6)	3843(3)	6335(5)	63(1)
C(27)	1142(7)	4191(3)	8804(5)	71(1)
C(28)	219(11)	4112(5)	9823(6)	110(2)
C(29)	2652(8)	4707(4)	9481(7)	106(2)
C(30)	−4342(7)	4827(4)	4483(7)	96(2)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

analogous tricarbonyl. J_{1-2} values are listed in Table 2. A small phosphorus coupling (2−3 Hz) to terminal diene protons is also evident in some cases.

5. Preparation of [(1-methylpentadienyl)Fe(CO)$_2$PPh$_3$]-PF$_6$ (31). Complex **2** (225 mg, 0.48 mmol) was dissolved in methanol (25 mL), and $NaBH_4$ (20 mg, 0.53 mmol) was added slowly at room temperature until infrared monitoring indicated that reaction was complete. The mixture was poured into water (20 mL), extracted with diethyl ether (3 × 15 mL), and dried over $MgSO_4$. Removal of solvent gave **26** as a yellow solid (190 mg, 87%). Mp: 132−134 °C. Anal. Calcd (found): C, 66.1 (65.8); H, 5.30 (5.18). Infrared (hexane): 1976, 1916 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): −0.15 (H2,5, m), 4.78 (H3,4, m), 3.41 (CH_2, m), 1.1 (Me, d). ^{13}C NMR ($CDCl_3$, 20 °C): 60.2, 61.3 (C2, C5), 83.6, 88.0 (C3, C4), 65.7 (CH_2), 18.4 (Me). ^{31}P NMR ($CDCl_3$, 20 °C): 66.7. Complex **26** was dissolved in diethyl ether (40 mL) and cooled to 0 °C. Aqueous HPF_6 (85%, 1 molar equiv) was added dropwise; after the mixture was stirred for 2 h, the product was isolated by filtration as a yellow powder (165 mg, 72%). Mp: 101 °C dec. Anal. Calcd (found): C, 52.0 (52.2); H, 4.00 (3.88). Infrared (CH_2Cl_2): 2042, 2002 cm^{-1}. ^{13}C NMR (CD_2Cl_2, −60 °C): 86.5 (4.8) (C1), 94.3, 100.5, 102.8 (C2−4), 61.3 (C5), 20.7 (Me), 205.0 (34.2) (CO_{basal}), 215.2 (14.7) (CO_{axial}). ^{31}P NMR (CD_2Cl_2, 20 °C): 60.5. Other [(dienyl)Fe(CO)$_2$L]PF$_6$ salts were prepared similarly. **30**: yield 79%; mp 185 °C dec. Anal. Calcd (found): C, 32.1 (32.0); H, 2.68 (2.81). Infrared (CH_2Cl_2): 2115, 2075, 2063 cm^{-1}. ^{13}C NMR (CD_2Cl_2, 60 °C): 90.7 (C1), 95.5, 104.7, 105.1 (C2−4), 63.4 (C5), 20.9 (Me), 199.4, 200.2 (CO_{basal}), 209.3 (CO_{axial}). **32**: yield 91%; mp 197 °C dec. Anal. Calcd (found): C, 28.6 (28.7); H, 3.93 (3.93). Infrared (CH_2Cl_2): 2055, 2011 cm^{-1}. ^{13}C NMR (CD_2Cl_2, −60 °C): 88.5 (8.0) (C1), 91.4, 101.1, 101.9 (C2−4), 60.3 (C5), 20.6 (Me), 202.5 (48.4) (CO_{basal}), 212.3 (28.5) (CO_{axial}).

Table 8. Atomic Coordinates (×10⁴) for 17a and Equivalent Isotropic Displacement Parameters (Å² × 10³)[a]

	x	y	z	U(eq)
Fe(1)	2410(1)	2991(1)	6580(1)	40(1)
P(1)	1542(2)	4348(2)	6830(1)	32(1)
O(1)	4842(8)	3367(6)	5773(5)	97(3)
O(2)	3862(13)	2710(7)	7967(6)	134(4)
C(1)	1194(12)	2825(8)	5650(7)	77(4)
C(2)	1817(9)	2003(7)	5847(7)	60(3)
C(3)	1673(11)	1689(8)	6559(8)	74(3)
C(4)	881(12)	2236(7)	7046(7)	87(4)
C(5)	2639(14)	1519(9)	5277(7)	96(4)
C(6)	3841(10)	3245(6)	6087(6)	55(3)
C(7)	3289(13)	2823(7)	7414(6)	75(3)
C(8)	−111(9)	4223(7)	7260(5)	40(2)
C(9)	−1261(8)	4189(7)	6826(5)	53(3)
C(10)	−2434(12)	3977(8)	7157(6)	70(3)
C(11)	−2516(13)	3789(9)	7904(7)	74(3)
C(12)	−1394(11)	3806(8)	8320(6)	72(3)
C(13)	−187(9)	4004(8)	8005(6)	53(3)
C(14)	2428(10)	5052(6)	7507(4)	40(2)
C(15)	1809(10)	5726(7)	7938(5)	48(3)
C(16)	2525(13)	6293(6)	8402(5)	62(3)
C(17)	3859(12)	6199(8)	8456(7)	70(3)
C(18)	4476(10)	5533(8)	8049(6)	55(3)
C(19)	3785(8)	4966(6)	7595(5)	43(2)
C(20)	1184(8)	5123(6)	6024(5)	38(2)
C(21)	2298(11)	5245(7)	5433(5)	47(3)
C(22)	1753(12)	5812(7)	4781(5)	62(3)
C(23)	1041(13)	6661(9)	4988(6)	82(4)
C(24)	−53(11)	6523(7)	5572(6)	62(3)
C(25)	521(10)	6015(6)	6244(5)	50(3)
C(26)	3660(9)	5556(7)	5729(5)	51(3)
C(27)	3747(12)	6498(7)	6093(6)	78(4)
C(28)	4693(11)	5481(12)	5097(7)	92(5)
C(29)	−1298(13)	6108(10)	5267(7)	102(5)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

^{31}P NMR (CD_2Cl_2, 20 °C): 152.7. **33a**: yield 81%; mp 84 °C dec. Anal. Calcd (found): C, 54.4 (55.0); H, 5.74 (6.17). Infrared (CH_2Cl_2): 2036, 1994 cm^{-1}. ^{13}C NMR (CD_2Cl_2, −60 °C): 86.2 (C1), 92.3, 101.6, 105.6 (C2−4), 63.2 (C5). ^{31}P NMR (CD_2Cl_2, 20 °C): 60.9. **33b**: yield 85%; mp 93 °C dec. Anal. Calcd (found): C, 54.4 (54.9); H, 5.74 (5.83). Infrared (CH_2Cl_2): 2036, 1994 cm^{-1}. ^{13}C NMR (CD_2Cl_2, −60 °C): 86.5 (C1), 93.6, 101.6, 106.5 (C2−4), 65.3 (C5). ^{31}P NMR (CD_2Cl_2, 20 °C): 65.8.

6. Reaction of 3 with MeMgI. Complex **3** (0.47 g, 1.0 mmol) was stirred at −78 °C in diethyl ether (10 mL), and MeMgI solution (350 μL of a 3 M solution in diethyl ether, 1.1 mmol) was added by syringe. After it was warmed to room temperature, the solution was hydrolyzed with saturated NH_4Cl (30 mL), extracted with diethyl ether (3 × 30 mL), and dried with $MgSO_4$. The crude product (0.34 g, 72% yield of a 1.9:1 mixture of **40** and **41**) was separated by Chromatotron using 1/4 ethyl acetate/60−80 °C petroleum ether to give **41** and **40** in order of elution as yellow solids. Complex **41**: mp 134−136 °C. Anal. Calcd (found): C, 66.7 (66.5); H, 5.56 (5.61). Infrared (hexane): 1981, 1919 cm^{-1}. ^{1}H NMR (C_6D_6, 20 °C): 0.06 (H2, dd), 4.67 (H3, m), 4.71 (H4, br), −0.55 (H5, br), 3.60 (*CH*Me, m), 1.18 (Me, d), 1.22 (CH*Me*, d). ^{31}P NMR (CD_2Cl_2, 20 °C): 66.2. **40**: mp 40−43 °C. Anal. Calcd (found): C, 66.7 (66.9); H, 5.56 (5.63). Infrared (hexane): 1973, 1915 cm^{-1}. ^{1}H NMR (C_6D_6, 50 °C): −0.07 (H2, H5, br), 5.32 (H3, br), 4.70 (H4, dd), 3.08 (*CH*Me, m), 1.01 (Me, d), 0.99 (CH*Me*, d). ^{31}P NMR (CD_2Cl_2, 20 °C): 66.2.

Reaction of **3** with MeLi·LiBr (1.5 M in diethyl ether) under the same conditions gave a 3.2:1 mixture of **40** and **41** (94% yield).

Reactions of **2** were performed similarly. Using MeMgI, a 1:2.5 mixture of **38** and **39** was obtained (79%). Separation by Chromatotron (1:4 ethyl acetate/60−80 °C petroleum ether) gave **39** and **38** as yellow solids in order of elution. **39**: infrared (hexane) 2043, 1973 cm^{-1}; ^{1}H NMR (C_6D_6, 20 °C) 0.68 (H2, m), 4.58 (H3, dd), 4.33 (H4, dd), 0.58 (H5, m), 3.39 (*CH*Me, m), 1.04 (Me, d), 0.98 (CH*Me*, d); ^{13}C NMR ($CDCl_3$, 20 °C) 58.4, 65.2 (C2, C5), 82.1, 86.5 (C3, C4), 19.3 (Me), 24.7, 71.1 (CHMe). **38**: infrared (hexane) 2043, 1973 cm^{-1}; ^{1}H NMR (C_6D_6, 20 °C) 0.40 (H2, t), 4.58 (H3, dd), 4.29 (H4, dd), 0.32 (H5, m), 3.28 (*CH*Me, m), 1.03 (Me, d), 1.13 (CH*Me*, d); ^{13}C NMR ($CDCl_3$, 20 °C) 58.1, 69.6 (C2, C5), 80.3, 85.3 (C3, C4), 19.1 (Me), 24.7,

Table 9. Atomic Coordinates (×10⁴) for 23 and Equivalent Isotropic Displacement Parameters (Å² × 10³)[a]

	x	y	z	U(eq)
Fe(1)	6835(1)	7845(1)	4275(1)	33(1)
Fe(2)	3893(1)	6958(1)	657(1)	36(1)
P(1)	6453(1)	7807(1)	5494(1)	29(1)
P(2)	3142(1)	7211(1)	−698(1)	32(1)
O(1)	9246(4)	6842(4)	4619(3)	87(1)
O(2)	6101(4)	5638(2)	3509(2)	64(1)
O(3)	4262(3)	7390(3)	3022(2)	69(1)
O(101)	7426(3)	8067(3)	1520(3)	89(1)
O(102)	5601(4)	9121(2)	1695(2)	67(1)
O(103)	2033(4)	7097(4)	1343(2)	92(1)
C(1)	10195(5)	7711(5)	6094(3)	73(1)
C(2)	9427(4)	7583(4)	5155(3)	61(1)
C(3)	8888(3)	8355(3)	4898(2)	46(1)
C(4)	8486(4)	8449(3)	4025(3)	50(1)
C(5)	7809(4)	9070(3)	3770(2)	48(1)
C(6)	7517(4)	9552(3)	4393(3)	47(1)
C(7)	6600(5)	10069(3)	4098(3)	64(1)
C(8)	6442(4)	6502(3)	3864(2)	42(1)
C(9)	5284(4)	7592(3)	3534(2)	44(1)
C(10)	7274(3)	9118(2)	6245(2)	33(1)
C(11)	6624(3)	9737(3)	6302(2)	40(1)
C(12)	7294(4)	10761(3)	6819(3)	49(1)
C(13)	8630(4)	11182(3)	7296(3)	52(1)
C(14)	9282(4)	10581(3)	7240(3)	52(1)
C(15)	8618(3)	9557(3)	6726(2)	44(1)
C(16)	6940(3)	6956(2)	6181(2)	33(1)
C(17)	7244(4)	7158(3)	7065(2)	48(1)
C(18)	7529(4)	6461(3)	7564(2)	55(1)
C(19)	7497(4)	5539(3)	7181(3)	49(1)
C(20)	7168(5)	5311(3)	6305(3)	55(1)
C(21)	6891(4)	6014(3)	5815(2)	47(1)
C(22)	4722(3)	7319(2)	5357(2)	32(1)
C(23)	3954(3)	7736(3)	4826(2)	39(1)
C(24)	2642(3)	7360(3)	4689(3)	46(1)
C(25)	2079(3)	6562(3)	5078(3)	52(1)
C(26)	2848(4)	6152(3)	5617(3)	49(1)
C(27)	4155(3)	6525(3)	5753(2)	40(1)
C(101)	7280(6)	7547(5)	112(5)	92(2)
C(102)	6766(4)	7459(3)	806(4)	61(1)
C(103)	5450(3)	6601(3)	609(3)	47(1)
C(104)	5092(4)	6331(3)	1323(3)	53(1)
C(105)	3791(4)	5621(3)	1151(3)	56(1)
C(106)	2876(4)	5244(3)	292(3)	53(1)
C(107)	1437(4)	4613(4)	85(4)	75(2)
C(108)	4957(4)	8297(3)	1261(2)	45(1)
C(109)	2740(4)	7050(4)	1043(2)	54(1)
C(110)	2091(3)	7905(2)	−894(2)	36(1)
C(111)	1111(3)	7631(3)	−567(2)	44(1)
C(112)	349(4)	8173(3)	−680(3)	57(1)
C(113)	526(4)	8988(3)	−1124(3)	62(1)
C(114)	1464(4)	9245(3)	−1467(3)	60(1)
C(115)	2242(4)	8721(3)	−1354(3)	48(1)
C(116)	4372(3)	8017(3)	−1093(2)	39(1)
C(117)	4560(4)	1056(3)	539(2)	46(1)
C(118)	3644(4)	392(3)	823(3)	58(1)
C(119)	3759(5)	651(4)	1655(3)	71(1)
C(120)	4813(6)	1537(4)	2213(3)	78(2)
C(121)	4242(5)	7790(4)	−1940(3)	62(1)
C(122)	2168(3)	5994(3)	−1556(2)	39(1)
C(123)	853(4)	5640(4)	−2027(3)	63(1)
C(124)	143(5)	4680(4)	−2639(4)	82(2)
C(125)	751(5)	4074(4)	−2795(4)	71(1)
C(126)	2055(4)	4426(4)	−2342(3)	59(1)
C(127)	2758(4)	5365(3)	−1721(3)	52(1)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

69.9 (CHMe). Using MeLi, a 1:1.2 mixture of **38** and **39** was obtained (98%).

Reaction of **5a** with MeMgI under the same conditions gave a single product (**42a**) as a yellow solid (67% yield). **42a**: mp 103–106 °C. Anal. Calcd (found): C, 67.9 (67.7); H, 7.47 (7.59). Infrared (hexane): 1963, 1899 cm^{-1}. ^{1}H NMR (C_6D_6, 60 °C): −0.63 (H2, H5, br), 5.17 (H3, dd), 4.73 (H4, dd), 3.79 (*CH*Me, m), 1.13 (Me, d), 1.03 (CH*Me*, d). ^{31}P NMR (CD_2Cl_2, 20 °C): 69.8 (br).

NaBH$_4$ Reduction of 3. Complex **3** (0.25 g, 0.52 mmol) was stirred at 0 °C in MeOH (15 mL). $NaBH_4$ (0.26 g, 6.6 mmol) was added, and the mixture was warmed to room temperature. After the mixture was stirred for 2 h, water (50 mL) was added; the product was extracted with diethyl ether (3 × 30 mL) and dried over $MgSO_4$. Chromatotron chromatography (1/4 ethyl acetate/60–80 °C petroleum ether) gave **41** as a yellow solid (0.22 g, 89%).

8. LiAlH$_4$ Reduction of 16a. Complex **16a** (0.12 g, 0.22 mmol) was stirred at −10 °C in diethyl ether (15 mL). $LiAlH_4$ (4 mg, 0.1 mmol) was added and the reaction monitored to completion by infrared sampling. Water (50 mL) was added, and the product was extracted wtih diethyl ether (3 × 30 mL) and dried over $MgSO_4$. The crude product (a 1:2 mixture of **42a** and **43a** contaminated by free phosphine) was purified by Chromatotron (1/9 ethyl acetate/60–80 °C petroleum ether) to give **43a** (27 mg, 29%) and **42a** (13 mg, 14%) in order of elution. Complex **43a**: mp 66–71 °C. Anal. Calcd (found): C, 67.9 (66.6); H, 7.47 (8.06). Infrared (hexane): 1967, 1905 cm^{-1}. ^{1}H NMR (C_6D_6, 60 °C): −0.62 (H2, br), 4.59 (H3, m), 4.74 (H4, m), −0.84 (H5, br), 3.50 (*CH*Me, m), 1.17 (Me, d), 1.06 (CH*Me*, d); ^{31}P NMR (CD_2Cl_2, 20 °C): 72.3 (br).

Comments similar to those above apply to coupling constants for complexes **38–43**: $J_{2\text{-CH}} \approx J_{\text{CH-Me}} \approx 6.2$–$6.4$ Hz.

9. Crystallography. Data were collected on an Enraf-Nonius CAD4 diffractometer. Structures were solved by Patterson methods (SHELX76)[42] and refined by full-matrix least squares (SHELXL-93).[43] Data were corrected for Lorentz and polarization effects but not for absorption. Non-hydrogen atoms were refined anisotropically. Except for the hydrogens on C4 of complex **15b**, which were located and refined, all hydrogens were included in calculated positions with common thermal parameters. For complexes **14a** and **23**, there are two essentially superposable molecules in each asymmetric unit. Crystallographic data are given in Table 5 and atomic coordinates in Tables 6–9.

Supplementary Material Available: Tables giving crystal data, thermal parameters for non-H atoms, bond distances and angles, and positional parameters for H atoms and figures giving the atom labeling for **14a**, **15b**, **17a**, and **23** (43 pages). Ordering information is given on any current masthead page.

OM940360T

(42) Sheldrick, G. M. SHELX86, A Computer Program for Crystal Structure Determination; University of Gottingen, Gottingen, Germany, 1986.

(43) Sheldrick, G. M. SHELXL-93, A Computer Program for Crystal Structure Determination; University of Gottingen, Gottingen, Germany, 1993.