Reactivity of (Pentadienyl)iron(1+) Cations: Nucleophilic Addition by Phosphines Is Reversible in **Certain Cases**

William A. Donaldson,* Lewei Shang, Muthukumar Ramaswamy, Christine A. Droste, and Chunlin Tao

Department of Chemistry, Marquette University, P.O. Box 1881, Milwaukee, Wisconsin 53201-1881

Dennis W. Bennett

Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201

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The reaction of (pentadienyl) $Fe(CO)_3^+$ cations 1, 5, and 11 with phosphines was examined. At short reaction times, attack of PPh₃ on 1a proceeds at both the unsubstituted and substituted pentadienyl termini to give 2a and 3a, respectively (2:1); however, over a period of ca. 21 h, the minor product **3a** isomerizes to the more thermodynamically stable **2a**. As the steric bulk of the 1-substituent is increased from methyl to ethyl (1b), kinetic attack by PPh_3 occurs exclusively at the unsubstituted pentadienyl terminus. The complex 2a was characterized crystallographically, and the stereochemistry of PPh₃ attack was established to be opposite to $Fe(CO)_3$ by use of a stereoselectively labeled cation, d_{exo} -1a. The reaction of PPh₃ with 11 initially gives E,Z-12, which isomerizes to E,E-12 over a 22 h period. Reaction with 5 with (S)-neomenthyl)diphenylphosphine gives two optically active diastereomers, 15a and 15b (3:2 ratio); fractional crystallization gives 15a in greater than 80% mass recovery. In solution, pure 15a isomerizes to a mixture of 15a and 15b (3:2). The interconversions of **3a** to **2a**, of E,Z-12 to E,E-12, and of **15a** and **15b** are rationalized by reversible phosphine addition.

Introduction

While $(\eta^5$ -pentadienyl)iron(1+) cations (1) were first prepared more than 30 years ago,¹ the reactivity of these complexes is of renewed interest.² The addition of phosphines to 1 to generate dienylphosphonium salts 2 was initially examined by McArdle and Sherlock³ and later extended by Salzer and Hafner.⁴ Both groups reported that nucleophilic attack occurs at the less hindered pentadienyl terminus to give E,Z-diene complexes, which can subsequently isomerize in solution to the correspondingly more stable E,E-diene complex (Scheme 1). The structural assignment of **2** was based on NMR spectral data. The regiochemical assignment was further corroborated by X-ray crystal structure of the pentaene complex generated from 2a via Wittig olefination.⁵ More recently, Grée has reported the use of phosphonium salts of this type for the preparation of Fe(CO)₃-complexed analogs of LTA₄.⁶ As part of our study of the applications of (pentadienyl)iron(1+) cations to organic synthesis, we have examined the reactivity of 1,2- and 1,4-disubstituted (pentadienyl)iron(1+)cations with phosphine and other heteroatom nucleophiles.⁷ We herein report on a detailed study of the title reaction, including an examination of the stereochemistry and reversibility of nucleophilic attack.⁸

Results and Discussion⁹

The cations 1a-e and 5 were prepared according to literature procedures.^{1,10} Reaction of 1a with PPh₃ (CH₂Cl₂, 21 h, 91%) gave the dienylphosphonium salt **2a**, as has been previously reported.^{3,4} However, monitoring this reaction by ¹H NMR spectroscopy (CD_3NO_2) indicated the initial formation of a mixture of **2a** and **3a** (ca. 2:1). Over a period of 24-42 h, the signals for 3a disappear, while the signals for 2a increase in intensity with respect to the CD₂HNO₂ signal. Likewise, precipitation of the reaction mixture of 1a with PPh_3 (CH₂Cl₂, 1 h) gave a solid which was identified as a mixture of 2a and 3a by ¹H NMR spectroscopy. Upon dissolution of this mixture in acetone- d_6 or CDCl₃, the slow (ca. 24 h) interconversion of 3a into 2a is again

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observed. Product 2a was identified by comparison of its spectral data with the literature values.^{3,4}



The assignment of **3a** as a ((3(Z),5-hexadien-2-y))triphenylphosphonium)Fe(CO)₃⁺ salt is based upon its ¹H NMR spectral data. In particular, the three-proton doublet of doublets at δ 1.56 ppm, exhibiting a large ³¹P-¹H coupling (18.3 Hz), indicates that the PPh₃⁺ functionality is attached next to the methyl substituent. In addition, the presence of signals at δ 2.38, 2.25, and 1.76 ppm (H3, H6_{exo}, and H6_{endo}, respectively) is characteristic of the (3(Z),5-hexadien-2-yl)Fe(CO)₃ group.

Our results indicate that there is little kinetic selectivity for nucleophilic attack of PPh₃ at either the unsubstituted or methyl-substituted pentadienyl termini of **1a** ($\Delta\Delta G^{\ddagger} \approx 0.4$ kcal/mol) and that interconversion of **3a** to the more thermodynamically stable **2a** over an extended reaction time is responsible for the reported^{3,4,11} isolation of **2a** as the sole product. In order to examine the mechanism of this process, the relative stereochemistry of attack by PPh₃ and of the interconversion was examined.

The reaction of (cyclohexadienyl)iron(1+) cation with PPh₃ has been shown unambiguously by X-ray crystallographic analysis to occur on the face opposite to the iron.¹² McArdle and Sherlock have previously noted³ that the diastereotopic methylene protons $H1_a$ and $H1_b$ of **2a** appear well separated in its ¹H NMR spectrum (δ 3.4 and δ 4.1 ppm) and that these protons have conspicuously different coupling constants with H2 (ca. 13 and 3.5 Hz, respectively). The difference in these coupling constants prompted an examination of the molecular structure of 2a. The structure of 2a was solved crystallographically. There are two, roughly mirror image, molecules per unit cell. The packing diagram is shown in Figure 1. The ORTEP II¹³ perspective views of the two asymmetric molecules, with the crystallographic numbering schemes, are given in Figures 2 and 3. Both display the 2(Z), 4(E) stereochem-



Figure 1. Crystal-packing diagram of 2a.



Figure 2. ORTEP II drawing of $(\eta^4$ -CH₃CH=CHCH=CHCH₂PPh₃⁺)Fe(CO)₃PF₆⁻ (**2a**, molecule I).

istry previously assigned^{3,4} on the basis of ¹H NMR spectra data. Selected bond distances and bond angles are given in Table 1. The two mirror image molecules exhibit equivalent bond distances within error limits. The bond distances and angles of the (diene)Fe(CO)₃ fragment of **2a** are in good agreement with those for other complexes reported in the literature.¹⁴ The torsional angles for H1a-C1-C2-H2 and for H1_b-C1-C2-H2 are respectively $159 \pm 6^{\circ} (-140 \pm 5^{\circ})$ and $38 \pm$

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Figure 3. ORTEP II drawing of $(\eta^4$ -CH₃CH=CHCH=CHCH=CHCH₂PPh₃⁺)Fe(CO)₃PF₆⁻ (2a, molecule II).

Table 1. Selected Bond Distances and BondAngles for the Two Molecules in the Unit Cellof $2a^a$

molecule 1		molecule II					
Bond Distances (Å)							
Fe1-C2	2.13(6)	Fe2-C32	2.12(4)				
Fe1-C3	1.93(3)	Fe2-C33	2.00(6)				
Fe1-C4	2.04(4)	Fe2-C34	1.88(7)				
Fe1-C5	2.04(5)	Fe2-C35	2.09(6)				
Fe1-C7	1.93(7)	Fe2-C38	1.67(3)				
Fe1-C8	1.75(4)	Fe2-C37	1.82(6)				
Fe1-C9	1.69(6)	Fe2-C39	1.77(7)				
P3-C1	1.86(4)	P4-C31	1.77(4)				
C1-C2	1.57(6)	C31-C32	1.50(5)				
C2-C3	1.47(7)	C32-C33	1.46(7)				
C3-C4	1.42(8)	C33-C34	1.31(6)				
C4-C5	1.33(6)	C34-C35	1.31(7)				
C5-C6	1.68(10)	C35-C36	1.55(6)				
C7-O7	0.98(8)	C37-O37	1.13(7)				
C8-O8	1.19(5)	C38-O38	1.22(4)				
C9-O9	1.23(8)	C39-O39	1.12(8)				
Bond Angles (deg)							
P3-C1-C2	107(3)	P4-C31-C32	119 (3)				
C1-C2-C3	120(4)	C31-C32-C33	126(4)				
C2-C3-C4	122(4)	C32-C33-C34	120(5)				
C3-C4-C5	117(5)	C33-C34-C35	123(5)				
C4 - C5 - C6	111(5)	C34-C35-C36	114(4)				
C1-C2-Fe1	115(4)	C31-C32-Fe2	121(3)				
C6-C5-Fe1	123(3)	C36-C35-Fe2	118(4)				
Fe1-C7-O7	173(5)	Fe2-C37-O37	173(5)				
Fe1-C8-O9	175(4)	Fe2-C38-O38	176(3)				
Fe1-C9-O9	174(4)	Fe2-C39-O39	179(6)				
C7-Fe1-C8	101(2)	C37-Fe2-C38	103(2)				
C7-Fe1-C9	87(3)	C37-Fe2-C39	98 (3)				
C8-Fe1-C9	103(2)	C38-Fe2-C39	88(2)				

 a Estimated standard deviations in this and all subsequent tables are given in parentheses.

 $3^{\circ}(-23 \pm 3^{\circ})$ for molecule I (molecule II). Since rotation about the C1-C2 bond would bring the PPh₃ group into steric interaction with the remainder of the molecule, we propose that the solution structure of **2a** is relatively similar to that found in the solid state. On this basis, the upfield signal (δ 3.34) which exhibits a larger H1-H2 coupling (J = 12.9 Hz) is assigned to the methylene proton which has the greater torsional angle with respect to H2 (i.e. H1_a). The downfield signal (δ 4.07, J = 3.5 Hz) is assigned to the methylene proton with the lesser torsional angle (H1_b).

The molecular structure of 2a has the PPh₃⁺ oriented opposite to Fe(CO)₃ in the solid state. However, the relative positions of the PPh₃⁺ and Fe(CO)₃ groups cannot be unambiguously interpreted to mean that nucleophilic attack occurs in an exo fashion, since endo



Figure 4. Partial ¹H NMR spectra of **2a** and *d*-**2a** (300 MHz, acetone- d_6).



attack followed by rotation about the C1-C2 bond would produce the same structure. For this reason, a stereoselective isotopically labeled pentadienyl cation was prepared (Scheme 2). Reduction of (sorbaldehyde)Fe-(CO)₃ with NaBD₄ in THF gave a mixture of isotopically labeled alcohols 4 in a 77:23 diastereomeric ratio (dr), as determined by integration of the diastereotopic methylene proton signals. It was not possible at this point to determine which was the major diastereomer. Treatment of the deuterium-labeled alcohols with HPF₆/ Ac₂O gave the stereoselectively labeled pentadienyl cation d_{exo}-1a (75:25 dr). Integration of the H1_{exo} signal at δ 3.50 (d, J = 9 Hz) and H1_{endo} at δ 2.17 (d, J = 13Hz) established the ratio as well as the d_{exo} stereochemistry of the major diastereomer.

Reaction of d_{exo} -1a with PPh₃ (CH₂Cl₂, 21 h, 97%) gave the labeled phosphonium salt d-2a (Scheme 2). Notably, the diastereotopic signals at δ 4.07 and at δ 3.34 of d-2a lack the geminal coupling (J = 14.7 Hz)(Figure 4) observed for the all-protio 2a; thus, each molecule contains one and only one deuterium. Integration of these two signals indicates a 28:72 dr. Because this diastereomeric ratio is nearly equal to that of the cation of d_{exo} -1a, it can be concluded that attack by PPh₃ occurs in a stereospecific fashion and, further, that the interconversion of **3a** to **2a** occurs in a stereospecific fashion with the same stereochemistry. Since we have previously assigned the signals at δ 3.34 and at δ 4.07 to H1_a and H1_b, respectively, then d-2a (major diastereomer) has the stereochemistry as indicated in Scheme 2. This establishes that attack by PPh₃ at the unsubstituted terminus of the *acyclic* pentadienyl ligand occurs on the face opposite to the $Fe(CO)_3$ group

(as had been previously demonstrated¹⁴ for (cyclohexadienyl) $Fe(CO)_3^+$). By analogy, we propose that attack by PPh_3 at the substituted terminus of 2 occurs on the face opposite to the $Fe(CO)_3$ group.

In comparison to 1a, ¹H NMR spectral monitoring of the reaction of 1b with PPh₃ (acetone- d_6 , 30 min) revealed only signals corresponding to 2b (eq 2). This



phosphonium salt could be isolated in excellent yield using the standard protocol ($CH_2Cl_2 > 20$ h). In general, the steric bulk of an ethyl substituent is not much greater than that of a methyl group. However, we have previously proposed that the methyl group of an ethyl substituent on the pentadienyl ligand is oriented away from the $Fe(CO)_3$ group, in order to minimize steric interactions. In this orientation, the ethyl group will present considerably greater steric hindrance to attack on the pentadienyl ligand on the face opposite to the metal. The reactions of 1c-e with PPh₃ (CH₂Cl₂, 16-24 h) gave 2c-e (eq 2). In each case, the product arises from nucleophilic attack at the unsubstituted pentadienvl terminus. It is of interest to note that nucleophilic attack by P(OMe)₃ on 1d was previously reported to occur at both C5 and C2.15 Complexes 2b-e are assigned the 2(Z), 4(E) stereochemistry by comparison of their ¹H NMR spectral data with those of 2a. In particular, the signals for H3 appear as a broad triplet (J ca. 6.1), while signals for H4 appear as a doublet of doublet (J ca. 5.1, 9.0). The ¹H NMR spectra of 2b-eexhibit chemical shifts and coupling constants for H1_a and $H1_b$ which are similar to those of **2a**.

The reaction of 5 with PPh₃ gave the (Z)-dienylphosphonium salt 6 (91%, Scheme 3). The Z olefinic geom-



etry was assigned on the basis of its ¹H NMR spectral data. In particular, the signal at δ 1.40 ppm is consistent with a methyl group in the exo orientation at C2.

McArdle and Sherlock have reported slow isomerization of the complex E, Z-2a to the more thermodynamically stable E, E complex in CDCl₃ solution;³ Salzer and Hafner reported E, Z to E, E isomerization only in CD₃-OD/CD₃ONa.⁴ The latter authors have proposed that 2a undergoes reversible deprotonation to generate the ylide E,Z-7. Isomerization of the ylide E,Z-7 to E,E-7may be rationalized by delocalization of the ylide electron density onto the metal. Reprotonation of E, E-7gives the E, E-dienylphosphonium salt (Scheme 1). In our hands, the E,Z complexes 2a-d were stable in acetone- d_6 at 23 °C for up to 6 h, as were 2e and 6 in hot acetone- d_6 (60 °C, 24 h). In comparison, heating a

sample of 6 in the presence of tris(p-methoxyphenyl)phosphine $(P(Anis)_3)$ gave the new phosphonium salt 8 (88%, Scheme 3). The spectral data for 8 are similar to those for 6. Furthermore, monitoring of the reaction of **6** with 1b by ¹H NMR spectroscopy (acetone- d_6 , 10 h) indicated the disappearance of signals for 6 and 1b and the appearance of signals corresponding to 5 and 2b (eq 2). In comparison, monitoring of the reaction of 5 and **2b** (acetone- d_6 , 25 h) showed no evidence for the formation of 6 or 1b (eq 3).



The interconversion of 3a to 2a, the transformation of 6 to 8 in the presence of $P(Anis)_3$, and phosphine exchange between 6 and 1b may be rationalized by a single mechanism. We propose that nucleophilic attack of PPh_3 on (pentadienyl)Fe(CO)₃⁺ cations is reversible, in certain cases. The situations where this attack is reversible are where there is steric hindrance between substituents present on the dienvl ligand and the triphenylphosphine group. Other instances of reversible nucleophilic addition to (pentadienyl)iron(1+) cations have been previously reported. For example, addition of $CpMo(CO)_3^-$ to 1a at -78 °C has been reported to give the bimetallic diene complex E, Z-9.¹⁶ This reaction has been shown to be reversible; equilibration of E, Z-9at room temperature leads to the bimetallic diene complex E.E.9 (eq 4). Moreover, reaction of E.Z.9 with PPh_3 leads to the formation of **2a**.



The 1,2,5-trisubstituted pentadienylFe(CO)₃ cation 11 $(\mathbf{R} = \mathbf{M}\mathbf{e})$ was prepared by protonation¹⁷ of the known triene complex 10.¹⁸ The reaction of 11 with PPh₃ was monitored by ¹H NMR spectroscopy (CD_3NO_2). At short reaction time (ca. 5 min) formation of E,Z-12 was observed. Over a period of 22 h, the signals for E,Z-12slowly disappeared and were replaced by the signals for E,E-12. E,E-12 could be isolated from the reaction of 11 with PPh₃ over an extended period (CH_2Cl_2 , 21 h; Scheme 4). The structural assignments for both isomers of 12 are based on their ¹H NMR spectral data. In particular, the presence of only a single downfield

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15b

(6)

R* = (S)-neomenthyl

Scheme 4



(82%)

nonaryl doublet at ca. δ 4.7 and signals at ca. δ 1.8 (s, 3H) and 1.5 (d, 3H) are characteristic of the type of dienyl fragment present in structure 12.7b The signals for H4 and H1 of the initially formed isomer appear at δ 2.02 and 2.52, while those for H4 and H1 of the final isomer appear at δ 0.55 and 1.39, thus supporting the assignments as E,Z-12 and E,E-12, respectively.

Initial reaction of PPh₃ with 11 must occur on the cisoid form of the cation, at the C5 (i.e. isopropylsubstituted) pentadienyl terminus. It should be noted that reaction of PPh₃ with the structurally similar cation 13 (R = H) has been reported to occur at the C1 (methyl substituted) pentadienyl terminus.⁴ Apparently the directing effect of the methyl group at C2 in 11 is sufficiently greater than that of the isopropyl substituent at the pentadienyl terminus. Since isomerization of E,Z-12 to E,E-12 occurs under neutral conditions, a mechanistic alternative to that of Salzer and Halfner is proposed. The isomerization involves reversible attack of PPh_3 on cation 11, followed by slow isomerization of the cisoid form of 11 to the less stable transoid form (Scheme 4). Nucleophilic attack of PPh₃ on the transoid form of 11 gives the thermodynamically more stable E, E-12. The reaction of freshly prepared E, Z-12 with tris(p-methoxyphenyl)phosphine was monitored by ¹H NMR spectroscopy (CD_3NO_2) . Over a period of 6 h, the signals for E.Z-12 were replaced by signals for E.Z-14(eq 5). The identity of the phosphonium salt E,Z-14 was



established by independent synthesis (reaction of 11 with $P(Anis)_3$). The rate of isomerization of E, Z-12 to E, E-12 is roughly comparable to the transformation of E,Z-12 into E,Z-14. This is consistent with an isomerization pathway which takes place via reversible phosphine attack.

The reaction of 5 with ((S)-neomenthyl)diphenylphosphine $(CH_2Cl_2, 22 h)$ gave a mixture of two diastereomers, 15a and 15b (3:2, eq 6). Diastereomers 15a and **15b** were identified as 2,4-dimethyl-2(Z),4-dienylphosphonium salts by comparison of their ¹H NMR spectral data with those of 6. The signals for H3 of the two diastereomers are well separated, and the ratio 15a: 15b was determined by integration of these signals. The ratio was not significantly affected by running this

reaction at 0 °C or at reflux. Slow, diffusion-controlled recrystallization of the mixture (CH₂Cl₂/ether) over 6 days gave 15a (81% mass recovery), as indicated by ¹H NMR spectroscopy. The structure of 15a, including its relative configuration, was solved crystallographically.⁸ This optically pure dienylphosphonium salt gave a rotation of $[\alpha]_D = +119.1$ (CH₃CN, after 15 min). Notably, if pure 15a is allowed to stand in CD₃CN (16 h), a mixture of 15a and 15b (3:2) is obtained, as indicated by ¹H NMR spectroscopy. Over this same period, the optical rotation decreases to a constant value of $[\alpha]_D = +41.7$ (CH₃CN). This implies a calculated rotation for 15b of $[\alpha]_D = ca. -74 (CH_3CN)$ (the rotations of 15a and 15b are not of equal magnitude, since they are diastereomers). The diastereoselectivity observed for addition of the chiral phosphine to 5 is the result of thermodynamic control. Isolation of greater than the equilibrium amount of 15a is rationalized on the basis of interconversion of 15a and 15b in solution and preferential crystallization of the major diastereomer, i.e. a second-order asymmetric transformation.¹⁹ We attribute the interconversion of diastereomers 15a and 15b to reversible phosphine addition. The present results are in sharp contrast to the reaction of (cyclohexadienyl) $Fe(CO)_3^+$ with ((S)-neomenthyl)diphenylphosphine.²⁰ For this latter reaction, the two possible diastereomers are found in an equimolar ratio, and while the diastereomers are separable by fractional crystallization, the individual diastereomers do not interconvert in solution. This provides yet another example of the differences in reactivity of acyclic (pentadienyl) $Fe(CO)_3^+$ cations and (cyclohexadienyl)Fe- $(CO)_3^+$ cations.

15a

In summary, for certain (pentadienyl) $Fe(CO)_3^+$ cations addition of phosphine nucleophiles has been shown to be a reversible process. This appears to be the case where there may be significant steric interactions between the phosphine and other substituents present on the pentadienyl ligand (i.e. 2,4-disubstituted or

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attack at a substituted pentadienyl terminus). This reversible process may be responsible for the isomerization of dienylphosphonium salts (both regio- and stereoisomeric) under mild conditions, and the reversibility can be utilized for the generation of optically pure dienylphosphonium salts via desymmetrization.

Experimental Section

General Data. For a description of general experimental conditions and instrumentation, see ref 7b. Tricarbonyl-(pentadienyl)iron cations 1a-e and 5 were prepared by literature methods.^{1,10} Tricarbonyl((5-phenyl-2(Z),4-pentadien-1-yl)triphenylphosphonium)iron hexafluorophosphate (2e) was prepared by the literature procedure.^{7b} The high-field ¹H NMR data are reported here. 2e: ¹H NMR (300 MHz, d_6 -acetone) δ 8.0–7.7 (m, 15H), 7.4–7.1 (m, 5H), 6.29 (dd, J = 5.3, 10.2 Hz, 1H), 5.57 (br t, J = 5.6 Hz, 1H), 4.30 (ddd, J = 3.4, 14.4, 15.6 Hz, 1H), 3.86 (d, J = 10.3 Hz, 1H), 3.68 (ddd, J = 12.2, 13.8, 15.5, 1H) (signal for H2 obscured by H₂O present in solvent).

Reaction of 1a with PPh₃. To a solution of **1a** (20 mg, 0.055 mmol) in CD_3NO_2 (0.4 mL) in a 5 mm NMR tube was added PPh₃ (20 mg, 0.076 mmol). The reaction mixture was monitored by ¹H NMR spectroscopy over a 42 h period (22 °C). Signals assigned to both **2a** and **3a** were initially observed (ca. 2:1 ratio). Over a period of 24-42 h, the signals for **3a** disappeared and the signals for **2a** increased in intensity.

On a preparative scale, to a solution of **1a** (0.69 g, 1.88 mmol) in CH_2Cl_2 (50 mL) was added PPh₃ (0.49 g, 1.87 mmol), and the mixture was stirred for 1 h. The reaction mixture was concentrated and triturated with ether until cloudy. A crystalline solid was obtained which was identified as a mixture of **2a** and **3a** (2:1) by ¹H NMR spectroscopy. Over a period of 24 h in solution, the signals for **3a** disappeared and only the signals for **2a** remained. **3a** (obtained as a mixture with **2a**): mp 146–160 °C (mixture); ¹H NMR (300 MHz, CD₃-NO₂) δ 5.46 (m, 1H), 5.18 (obscured by signal for **2a**), 3.12 (m, 1H), 2.38 (dt, J = 11.4, 9.3 Hz, 1H), 2.25 (dd, J = 3.6, 7.8 Hz, 1H), 1.76 (dd, J = 3.9, 9.9 Hz, 1H), 1.56 (dd, J = 6.6, 18.3 Hz, 3H). Anal. Calcd for $C_{27}H_{24}O_3FeP_2F_6$ (mixture of **2a** and **3a**): C, 51.62; H, 3.85. Found: C, 51.70; H, 4.00.

A pure sample of **2a** was prepared by stirring **1a** (1.00 g, 2.73 mmol) with PPh₃ (0.72 g, 2.75 mmol) in CH₂Cl₂ (20 mL) for 21 h. The reaction mixture was added to a large excess of Et₂O, and the resultant precipitate was collected by vacuum filtration and dried in vacuo to give 2a as a yellow solid: 1.56 g, 91%. 2a: mp 136-140 °C dec; IR (cm⁻¹, CH₂Cl₂) 2051, 1977, 1464; ¹H NMR (300 MHz, d_6 -acetone) δ 8.0–7.7 (m, 15H), 5.40 (dd, J = 5.0, 9.3 Hz, 1H), 5.32 (br t, J = 6.1 Hz, 1H), 4.07 (dt, J = 6.1J = 3.4, 14.9 Hz, 1H), 3.34 (dt, J = 14.7, 12.9 Hz, 1H), 2.62 (ddt, J = 4.9, 7.7, 11.7, 1H), 1.44 (d, J = 6.1 Hz, 3H), signalfor H5 obscured by H_2O present in solvent; ¹H NMR (300 MHz. CD_3NO_2) δ 8.0-7.7 (m, 15H), 5.32 (dd, J = 5.4, 9.6 Hz, 1H), 5.18 (br t, J = 6 Hz, 1H), 3.69 (ddd, J = 3.3, 13.5, 15.6 Hz, 1H), 2.96 (ddd, J = 12.0, 13.5, 15.3 Hz, 1H), 2.67 (qd, J = 6.0, 9.6 Hz, 1H), 2.52 (m, 1H), 1.48 (d, J = 6.0 Hz, 3H); ³¹P NMR $(24 \text{ MHz}, \text{CDCl}_3) \delta 23.7$. Anal. Calcd for $C_{27}H_{24}O_3\text{FeP}_2F_6$: C, 51.62; H, 3.85. Found: C, 51.18; H, 3.90.

Tricarbonyl(1-deuterio-2,4-hexadienol)iron (4). To a solution of tricarbonyl(2,4-hexadienal)iron (3.40 g, 14.4 mmol) in dry THF (30 mL) was added NaBD₄ (96 atom % D, 0.84 g, 20 mmol). The reaction mixture was stirred at room temperature for 24 h and then diluted with ether (15 mL) and H₂O (30 mL). After gas evolution ceased, the layers were separated and the aqueous layer was extracted with ether (2×15 mL). The combined ether layers were filtered through filter aid and dried (MgSO₄), and the solvent was evaporated to give the product as a yellow oil: 2.93 g, 85%. The ¹H NMR spectrum of this product was similar to that of the known all-proton analog^{1a} and indicated a 77:23 mixture of diastereomeric

deuterated alcohols. The ratio was determined from integration of the diastereotopic methylene protons at δ 3.60 and 3.70 ppm. Reduction of tricarbonyl(2,4-hexadienal)iron with NaBD₄ in dioxane gave similar results (74:26 dr, 79%), while reduction with NaBD₄ in CH₃OD gave considerably lower diastereoselectivity (58:42 dr, 89%).

Tricarbonyl(1-exo-deuterio-2,4-hexadienyl)iron Hexafluorophosphate (d_{exo} -1a). To a solution of 3 (2.93 g, 12.3 mmol) in Ac₂O (2 mL) at 0 °C was added dropwise an ice cold solution of HPF₆ (2.0 g) in Ac₂O (2 mL), and the mixture was stirred for 15 min. Dropwise addition of the mixture to excess ether (200 mL) resulted in the formation of a yellow precipitate. The ether was decanted, and the precipitate was washed with ether (2 × 100 mL) and dried in vacuo to afford 3 as a yellow solid: 2.92 g, 78%. d_{exo} -1a: ¹H NMR (60 MHz, CD₃NO₂) δ 6.93 (t, J = 6 Hz, 1H), 6.3–5.7 (complex m, 2H), 3.50 (br d, J = 9 Hz, 0.25 H), 3.25 (dq, J = 12, 6 Hz, 1H), 2.17 (d, J = 13 Hz, 0.75 H), 1.80 (d, J = 6 Hz, 3H).

General Procedure for Preparation of Dienylphosphonium Salts. To a solution of the tricarbonyl(pentadienyl)iron hexafluorophosphate in CH₂Cl₂ (ca. 20 mL) was added an equimolar amount of solid PPh₃. The reaction mixture was stirred for 16–24 h, the solvent was evaporated, the residue was dissolved in a minimal amount of CH₂Cl₂ (ca. 5 mL), and this solution was added dropwise to excess Et₂O (ca. 100–500 mL). The resultant precipitate was collected by vacuum filtration and dried in vacuo. The following dienylphosphonium salts were prepared in the above fashion.

Tricarbonyl((1-deuterio-2(Z),4(E)-hexadien-1-yl)triphenylphosphonium)iron Hexafluorophosphate (d-2a). The reaction of d_{exo} -1a (0.50 g, 1.36 mmol) with PPh₃ gave the phosphonium salt d-2a as a yellow solid: 0.83 g, 97%; mp 166–168 °C (foams); IR (cm⁻¹, KBr) 2365 w, 2334 w, 2056 s, 1976 s; ¹H NMR (300 MHz, d_6 -acetone) δ 8.0–7.7 (m, 15H), 5.40 (dd, J = 5.0, 9.3 Hz, 1H), 5.32 (br t, J = 6.1 Hz, 1H), 4.07 (dd, J = 3.4, 14.2 Hz, 0.28 H), 3.34 (br t, J = 12.6 Hz, 0.72H), 2.62 (m, 1H), 1.44 (d, J = 6.1 Hz, 3H), signal for H5 obscured by H₂O present in solvent; ³¹P NMR (24 MHz, CDCl₃) δ 23.2. Anal. Calcd for C₂₇H₂₃DO₃FeP₂F₆: C, 51.53; H, 4.00. Found: C, 51.56; H, 3.93.

Tricarbonyl((2(Z),4(E)-heptadien-1-yl)triphenylphosphonium)iron Hexafluorophosphate (2b). The reaction of 1b (1.14 g, 3.00 mmol) with PPh₃ gave phosphonium salt **2b** as a yellow solid: 1.87 g, 97%; mp 159–160 °C dec; IR (cm⁻¹, CH₂Cl₂) 2054, 1988; ¹H NMR (300 MHz, d_6 -acetone) δ 8.0–7.7 (m, 15H), 5.41 (dd, J = 5.0, 9.1 Hz, 1H), 5.35 (br t, J = 6.2 Hz, 1H), 4.10 (dt, J = 3.9, 14.9 Hz, 1H), 3.39 (dt, J = 14.9, 12.9 Hz, 1H), 2.79 (dt, J = 9.3, 6.8 Hz, 1H), 2.64 (m, 1H), 1.84 (m, 1H), 1.55 (ddq, J = 14.4, 7.2, 7.2 Hz, 1H), 1.06 (t, J = 7.3 Hz, 3H); ¹³C NMR (75 MHz, d_6 -acetone) δ 135.8, 134.7 ($J_{PC} = 9.7$ Hz), 131.0 ($J_{PC} = 12.1$ Hz), 118.9 ($J_{PC} = 83.6$ Hz), 95.6, 82.6, 69.5, 44.1 ($J_{PC} = 10.9$ Hz), 25.0 ($J_{PC} = 40.0$ Hz), 16.3; ³¹P NMR (24 MHz, CDCl₃) δ 23.0. Anal. Calcd for C₂₈H₂₆O₃-FeP₂F₆: C, 52.36; H, 4.08. Found: C, 52.39; H, 4.00.

Tricarbonyl((2(Z),4(E)-octadien-1-yl)triphenylphosphonium)iron Hexafluorophosphate (2c). The reaction of 1c (200 mg, 0.508 mmol) with PPh₃ gave phosphonium salt 2c as a yellow solid: 300 mg, 90%; mp 151–154 °C (foams); ¹H NMR (300 MHz, d_{6} -acetone) δ 8.0–7.7 (m, 15H), 5.42 (dd, J = 5.1, 9.0 Hz, 1H), 5.35 (br t, J = 6.5 Hz, 1H), 4.11 (ddd, J = 3.8, 14.2, 15.6 Hz, 1H), 3.34 (ddd, J = 12.1, 13.1, 15.3 Hz, 1H), 2.78 (m, 1H), 2.64 (m, 1H), 1.64 (m, 2H), 1.47 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H); ¹³C NMR (15 MHz, CDCl₃) δ 2096, 135.5, 133.5 ($J_{PC} = 8$ Hz), 130.6 ($J_{PC} = 11$ Hz), 117.3 ($J_{PC} = 84$ Hz), 95.3, 80.8 ($J_{PC} = 4$ Hz), 67.2, 40.9 ($J_{PC} = 12$ Hz), 37.6, 30.8, 25.0 ($J_{PC} = 43$ Hz), 13.9; ³¹P NMR (24 MHz, CDCl₃) δ 23.4. Anal. Calcd for C₂₉H₂₈O₃FeP₂F₆H₂O: C, 51.65; H, 4.48. Found: C, 51.00; H, 4.32.

Tricarbonyl((5-(methoxycarbonyl)-2(Z),4(E)-pentadien-1-yl)triphenylphosphonium)iron Hexafluorophosphate (2d). The reaction of 1d (500 mg, 1.22 mmol) with PPh₃ gave the phosphonium salt 2d as a yellow solid: 750 mg, 91%; mp 167–169 °C; ¹H NMR (300 MHz, d_6 -acetone) δ 8.0–7.7 (m, 15H), 6.01 (dd, J = 5.2, 8.7 Hz, 1H), 5.60 (br t, J = 5.4 Hz, 1H), 4.24 (dt, J = 3.2, 15.1 Hz, 1H), 3.64 (s, 3H), 3.40 (ddd, J = 12.1, 14.1, 15.3, 1H), 3.01 (m, partially obscured by H₂O present in solvent), 2.58 (dd, J = 1.0, 8.9 Hz, 3H); ¹³C NMR (75 MHz, d_6 -acetone) δ 174.2, 137.1, 135.9 ($J_{PC} = 9.8$ Hz), 132.1 ($JP_C = 12.2$ Hz), 119.9 ($J_{PC} = 84.2$ Hz), 95.6, 87.5 ($J_{PC} = 3.7$ Hz), 52.4, 48.1, 46.0 ($J_{PC} = 9.8$ Hz), 25.4 ($J_{PC} = 42.7$ Hz). Anal. Calcd for C₂₈H₂₄O₅FeP₂F₆: C, 50.02; H, 3.60. Found: C, 50.08; H, 3.57.

Tricarbonyl((2,4-dimethyl-2(Z),4-pentadien-1-yl)triphenylphosphonium)iron Hexafluorophosphate (6). The reaction of **5** (230 mg, 0.60 mmol) with PPh₃ gave phosphonium salt **6** as a yellow solid: 350 mg, 91%; mp > 185–187 °C; ¹H NMR (300 MHz, CD₃CN) δ 7.9–7.6 (m, 15H), 4.95 (s), 4.07 (dd, J = 12.2, 15.5 Hz), 2.86 (dd, J = 14.1, 15.5 Hz), 1.87 (d, J = 3.9 Hz), 1.72 (s, 3H), 1.40 (d, J = 2.1 Hz, 3H), 1.19 (d, J = 4.5 Hz); ¹³C NMR (75 MHz, CD₃CN) δ 211.4, 136.2 ($J_{PC} = 3.6$ Hz), 134.9 ($J_{PC} = 9.7$ Hz), 131.2 ($J_{PC} = 12.2$ Hz), 119.3 ($J_{PC} = 82.4$ Hz), 105.5, 93.1 ($J_{PC} = 3.7$ Hz), 58.7 ($J_{PC} = 13.3$ Hz), 46.3, 33.5, 31.4 ($J_{PC} = 35.1$ Hz), 24.4 An analytically pure sample of **5** was prepared by precipitation from a concentrated CH₂-Cl₂ solution by slow addition of ether. Anal. Calcd for C₂₈H₂₆O₃FeP₂F₆-C, 52.24; H, 4.08. Found: C, 52.24; H, 3.98.

Tricarbonyl((2,4-dimethyl-2(Z),4-pentadien-1-yl)tris(pmethoxyphenyl)phosphonium)iron Hexafluorophosphate (8). To a solution of 6 (0.15 g, 0.23 mmol) in acetone (20 mL) was added tris(p-methoxyphenyl)phosphine (0.08 g, 0.23 mmol). The solution was heated at reflux for 5 h, cooled, and added dropwise to ether (300 mL). The resultant precipitate was collected by vacuum filtration and dried in vacuo to afford 8 a yellow powder: 0.15 g, 88%; mp >174 °C dec; ¹H NMR (300 MHz, CD₃NO₂) δ 7.71 (dd, J = 9.0, 11.7 Hz), 7.27 (dd, J = 2.7, 8.9 Hz), 5.08 (s), 3.96 (m), 3.96 (s, 9H), 2.88 (dd, J = 0.9, 15.0Hz), 2.12 (s, 3H), 1.96 (d, J = 4.5 Hz), 1.87 (s, 3H), 1.52 (d, J= 2.1 Hz), 1.24 (d, J = 4.2 Hz); ¹³C NMR (75 MHz, CD₃NO₂) δ 212.1, 166.4 ($J_{PC} = 2.5 \text{ Hz}$), 137.2 ($J_{PC} = 10.9 \text{ Hz}$), 117.1 $(J_{\rm PC} = 13.4 \text{ Hz}), 110.4 (J_{\rm PC} = 90.9 \text{ Hz}), 105.8, 94.0 (J_{\rm PC} = 3.5 \text{ Hz})$ Hz), 59.9 ($J_{PC} = 12.2$ Hz), 56.9, 46.1, 33.8, 33.0 ($J_{PC} = 38.8$ Hz), 24.7. Anal. Calcd for $C_{31}H_{32}O_6FeP_2F_6$: C, 50.82; H, 4.41. Found: C, 50.77; H, 4.41.

Tricarbonyl((2-6- η^5)-3,7-dimethyl-2,4-octadien-5-yl)iron Hexafluorophosphate (11). The preparation of 11 utilized a modified procedure for the protonation of (triene)- $Fe(CO)_3$ complexes¹⁷ as follows. To tricarbonyl((2-5- η^4)-3,7dimethyl-2,4,6-octatriene)iron¹⁸ (3.80 g, 13.8 mmol) was added a solution of HPF_6 -Ac₂O (1:1, 10 mL). The mixture was allowed to stand for 1 h and was then added dropwise to excess ether (300 mL). The resultant precipitate was collected by vacuum filtration and dried in vacuo to afford 11 as a yellow solid: 4.04 g, 69%; mp >130 °C dec; IR (cm⁻¹, CH₂Cl₂) 2033, 1963; ¹H NMR (300 MHz, CD₃NO₂) δ 6.73 (d, J = 7.5 Hz, 1H), 5.78 (dd, J = 7.5, 12.6 Hz, 1H), 3.58 (dd, J = 9.0, 12.6, 1H), 2.66 (q, J = 6.0 Hz, 1H), 2.42 (s, 3H), 1.94 (m, 1H), 1.76 (d, J)= 6.0 Hz, 3H), 1.38 (d, J = 6.6 Hz, 3H), 1.19 (d, J = 6.6 Hz, 3H); ¹³C NMR (75 MHz, CD₃NO₂) δ 124.7, 103.0, 101.4, 93.1, 85.6, 37.8, 24.7, 24.0, 20.5, 17.2. This compound decomposes upon heating and did not give a satisfactory elemental analysis

Reaction of 11 with Triphenylphosphine. To a solution of **11** (0.02 g, 0.05 mmol) in CD₃NO₂ (1 mL) in an 5 mm NMR tube was added PPh₃ (0.01 g, 0.05 mmol). The reaction mixture was monitored by ¹H NMR spectroscopy over 20 h (22 °C). Signals assigned to the 4(Z),6(E)-dienylphosphonium salt (E,Z-12) were initially observed. E,Z-12: ¹H NMR (300 MHz, CD₃NO₂) δ 8.0–7.7 (m, 15H), 4.82 (d, J = 7.5 Hz, 1H), 3.27 (t, J = 13.5 Hz, 1H), 2.52 (m, 2H), 2.02 (dt, J = 12.9, 8.1 Hz, 1H), 1.80 (s, 3H), 1.53 (d, J = 6.3 Hz, 3H), 1.50 (d, J = 6.3 Hz, 3H), 0.47 (d, J = 6.9 Hz, 3H). Over a period of 20 h, these signals were replaced by those assigned to the 4(E),6(E)-isomer (E,E-12). A sample of E,E-12 was prepared by stirring **10** (0.15 g, 0.36 mmol) with PPh₃ (0.11 g, 0.42 mmol) in CH₂Cl₂ (12

Table 2. Crystallographic data for 2a

Table 2. Crystanog	aphic data for 20
ormula	C ₂₇ H ₂₄ O ₃ FeP ₂ F ₆
mol wt	628.27
cryst syst	triclinic
space group	P1
a (Å)	10.185(3)
b (Å)	10.866(5)
c (Å)	14.978(7)
a (deg)	74.39(4)
β (deg)	104.12(3)
γ (deg)	114.84(3)
$V(\dot{A}^3)$	1432.4(11)
Z	2
cryst size (mm)	0.20 imes 0.20 imes 0.25
monochromator	none
radiation wavelength (Å)	Mo Ka (Zr filtered)
temp (°C)	ambient
2θ range (deg)	35
no. of rflns measd	1858
no. of rflns obsd	1310
linear abs coeff (cm ⁻¹)	7.0
R	0.092
$R_{ m w}$	0.091

mL) for 21 h. The reaction mixture was added to a large excess of Et₂O, and the resultant precipitate was collected by vacuum filtration and dried in vacuo to give *E,E*-12 as a yellow solid: 0.19 g, 77%; mp 156–158 °C; IR (cm⁻¹, CH₂Cl₂) 2048, 1981; ¹H NMR (300 MHz, CD₃NO₂) δ 8.0–7.7 (m, 15H), 4.54 (d, *J* = 8.7 Hz, 1H), 3.35 (dd, *J* = 10.2, 13.5 Hz, 1H), 2.65 (m, 1H), 1.87 (s, 3H), 1.47 (d, *J* = 6.9 Hz, 3H), 1.44 (s, 3H), 1.39 (m, 1H), 0.55 (ddd, *J* = 3.9, 8.7, 11.1 Hz, 1H), 0.47 (d, *J* = 6.6 Hz, 3H); ³¹P NMR (120 MHz, CD₃NO₂) δ 25.9. An analytically pure sample was prepared by precipitation from a concentrated CH₂Cl₂ solution by slow addition of ether, followed by drying the yellow flakes in vacuo at 80 °C for 20 h. Anal. Calcd for C₂₉H₃₂O₃FeP₂F₆: C, 54.40; H, 4.71. Found: C, 54.21; H, 4.74.

Tricarbonyl((2,6-dimethyl-4(Z),6(E)-octadien-3-yl)tris-(p-methoxyphenyl)phosphonium)iron Hexafluorophosphate (E,Z-14). To a solution of 11 (0.24 g, 0.57 mmol) in CH₂Cl₂ (10 mL) was added P(Anis)₃ (0.21 g, 0.60 mmol). The reaction mixture was stirred for 21 h and then was added dropwise to excess hexanes (100 mL). The resultant precipitate was collected by vacuum filtration and dried in vacuo to afford E,Z-13 as a yellow solid: 0.38 g, 86%. E,Z-14: ¹H NMR (300 MHz, CD₃NO₂) δ 7.75 (dd, J = 9.0, 11.7 Hz, 6H), 7.25 (m, 6H), 4.83 (d, J = 7.8 Hz, 1H), 3.94 (s, 9H), 3.08 (t, J = 12.9 Hz, 1H), 2.49 (d, J = 6.0 Hz, 1H), 2.47 (m, 1H), 1.98 (m, 1H), 1.85 (s, 3H), 1.52 (d, J = 6.3 Hz, 3H), 1.47 (d, J = 6.9 Hz, 3H), 0.52 (d, J = 6.9 Hz, 3H).

Tricarbonyl((2(S),4(R))-dimethyl-2(Z),4-pentadien-1yl)((S)-neomenthyl)diphenylphosphonium)iron Hexafluorophosphate (15a). To a solution of 5 (0.19 g, 0.50 mmol) in CH₂Cl₂ (10 mL) was added ((S)-neomenthyl)diphenylphosphine (0.16 g, 0.50 mmol). The reaction mixture was stirred for 22 h, the solvent was evaporated, the residue was dissolved in CH_2Cl_2 (5 mL), this solution was added dropwise to excess Et_2O (100 mL), and the resultant precipitate was collected by vacuum filtration. The reprecipitation procedure was repeated a second time, and the product was dried in vacuo to afford 15a,b as a yellow solid: 0.29 g, 82%. Slow diffusion-controlled recrystallization of the mixture (0.16 g) from CH₂Cl₂/ether gave a single diastereomer, 15a: 0.13 g, 81% mass recovery. Over a period of 16 h in CD₃CN solution this isomerized to an equilibrium mixture of 15a and 15b (3:2). 15a: mp 190-192 °C; $[\alpha]_D = +119.1^\circ$ (CH₃CN, t = 15 min); ¹H NMR (300 MHz, CD_3CN) δ 8.1–7.6 (m, 10H), 4.31 (br s, 1H), 3.87 (dd, J = 11.115.6 Hz, 1H), 3.49 (m, 1H), 2.31 (dd, J = 12.3, 15.6 Hz, 1H), 2.26 (d, J = 4.8, 1H), 1.84 (m), 1.72 (s, 3H), 1.63 (m), 1.50 (m),1.38 (d, J = 2.1 Hz, 3H), 1.25 (dd, J = 0.9, 4.8, 1H), 0.97 (d, J = 0.9)= 6.3 Hz, 3H), 0.91 (d, J = 6.9 Hz, 3H), 0.46 (d, J = 6.6 Hz, 3H); ³¹P NMR (120 MHz, CDCl₃) δ 32.2, -143.2. Anal. Calcd for C₃₂H₄₀O₃P₂F₆Fe: C, 54.55; H, 5.68. Found: C, 53.55; H, 5.63. 15b: ¹H NMR (300 MHz, CD₃CN, partial) δ 4.39 (br s,

Table 3. Positional Parameters for the Two Molecules in the Unit Cell of 2a

molecule I			molecule II				
atom	x	У	2	atom	x	у	z
Fe1	-0.17710(0)	1.16590(0)	-0.39640(0)	Fe2	0.2202(9)	0.1892(8)	0.3625(6)
P 3	0.0005(13)	0.8191(11)	-0.2118(8)	P4	0.6101(13)	0.4803(11)	0.1833(8)
C1	-0.018(4)	0.990(4)	-0.248(2)	C31	0.440(4)	0.409(4)	0.224(3)
C2	-0.114(5)	0.992(5)	-0.346(4)	C32	0.426(4)	0.321(4)	0.321(3)
C3	-0.270(4)	0.969(4)	-0.356(2)	C33	0.402(5)	0.175(5)	0.347(3)
C4	-0.319(5)	1.031(4)	-0.306(3)	C34	0.280(5)	0.083(5)	0.314(3)
C5	-0.218(5)	1.132(5)	-0.263(3)	C35	0.189(5)	0.113(5)	0.242(3)
C6	-0.296(6)	1.220(5)	-0.231(4)	C36	0.045(5)	-0.010(5)	0.219(4)
C7	-0.287(6)	1.284(6)	-0.443(4)	C37	0.134(5)	0.308(5)	0.294(4)
C8	-0.000(5)	1.287(4)	-0.372(3)	C38	0.084(4)	0.058(4)	0.413(2)
C9	-0.188(6)	1.158(5)	-0.509(4)	C39	0.281(6)	0.253(5)	0.468(4)
07	-0.333(4)	1.351(4)	-0.470(2)	O37	0.074(4)	0.374(4)	0.246(3)
08	0.121(4)	1.370(3)	-0.362(2)	O38	-0.009(3)	-0.037(3)	0.4546(19)
O9	-0.183(4)	1.164(3)	-0.592(3)	O39	0.320(4)	0.292(4)	0.536(3)
C10	-0.175(2)	0.691(2)	-0.2354(19)	C40	0.748(3)	0.530(3)	0.2811(16)
C11	-0.272(2)	0.659(2)	-0.1732(19)	C41	0.732(3)	0.607(3)	0.3364(16)
C12	-0.419(2)	0.571(2)	-0.1930(19)	C42	0.844(3)	0.655(3)	0.4097(16)
C13	-0.468(2)	0.516(2)	-0.2750(19)	C43	0.970(3)	0.626(3)	0.4275(16)
C14	-0.370(2)	0.549(2)	-0.3373(19)	C44	0.985(3)	0.548(3)	0.3722(16)
C15	-0.224(2)	0.636(2)	-0.3174(19)	C45	0.874(3)	0.500(3)	0.2989(16)
C16	0.124(3)	0.814(3)	-0.2754(19)	C46	0.620(3)	0.632(2)	0.0962(16)
C17	0.142(3)	0.688(3)	-0.2489(19)	C47	0.493(3)	0.642(2)	0.0386(16)
C18	0.232(3)	0.664(3)	-0.2940(19)	C48	0.502(3)	0.759(2)	-0.0315(16)
C19	0.302(3)	0.765(3)	-0.3656(19)	C49	0.637(3)	0.866(2)	-0.0438(16)
C20	0.284(3)	0.891(3)	-0.3921(19)	C50	0.765(3)	0.856(2)	0.0139(16)
C21	0.194(3)	0.916(3)	-0.3470(19)	C51	0.756(3)	0.739(2)	0.0839(16)
C22	0.070(3)	0.793(3)	-0.0879(14)	C52	0.641(4)	0.363(3)	0.135(2)
C23	0.046(3)	0.659(3)	-0.0358(14)	C53	0.689(4)	0.400(3)	0.048(2)
C24	0.106(3)	0.640(3)	0.0591(14)	C54	0.717(4)	0.305(3)	0.015(2)
C25	0.190(3)	0.755(3)	0.1019(14)	C55	0.696(4)	0.174(3)	0.069(2)
C26	0.214(3)	0.888(3)	0.0497(14)	C56	0.648(4)	0.136(3)	0.156(2)
C27	0.154(3)	0.907(3)	-0.0452(14)	C57	0.620(4)	0.231(3)	0.189(2)
P1	0.4556(19)	0.7627(17)	0.3865(12)	P 2	1.1450(18)	1.3011(17)	-0.0562(11)
F1	0.551(5)	0.841(5)	0.319(3)	F 7	1.163(4)	1.253(4)	-0.140(2)
F2	0.356(6)	0.664(5)	0.460(4)	F8	1.139(3)	1.357(3)	0.030(2)
F3	0.598(5)	0.750(5)	0.448(3)	F9	1.264(4)	1.256(4)	0.005(3)
F4	0.333(5)	0.794(5)	0.327(3)	F10	1.035(4)	1.364(4)	-0.124(3)
F5	0.409(4)	0.638(4)	0.336(3)	F11	1.029(4)	1.161(4)	-0.031(2)
F6	0.499(4)	0.885(3)	0.436(2)	F12	1.263(4)	1.440(4)	-0.092(3)

1H), 3.74 (dd, J = 11.1, 15.6 Hz, 1H), 1.71 (s, 3H), 1.30 (d, J = 2.4 Hz, 3H), 0.99 (d, J = 6.3 Hz, 3H), 0.72 (d, J = 6.6 Hz, 3H), 0.49 (d, J = 6.9 Hz, 3H); ³¹P NMR (120 MHz, CDCl₃) δ 27.6, -143.2.

Crystallographic Analysis of Tricarbonyl((2(Z),4(E)hexadien-1-yl)triphenylphosphonium)iron Hexafluorophosphate. Golden yellow crystals of 2a were grown from a concentrated CH₂Cl₂ solution by slow addition of ether. The X-ray diffraction data were collected with a Picker diffractometer from a crystal of dimensions $0.20 \times 0.20 \times 0.25$ mm³. The unit cell dimensions were determined from 12 reflections in the range $4.83 \le 2\theta \le 9.77^{\circ}$. Crystal data, data collection parameters, and results of the analysis are listed in Table 2. Data were globally sorted and collected using PCXTL,²¹ and data handling, reduction, and analysis were performed using NRCVAX.²² The structure was solved by direct methods using SHELXS-86.²³ All heavy atoms with the exception of iron were refined isotropically using SHELX-76.²⁴ Hydrogen atoms were allowed to ride with the heavy atoms to which they were bonded. A single hydrogen isotropic thermal parameter was réfined to a value of 0.255 Å². Data for this structure were initially collected assuming a centrosymmetric structure with one molecule per asymmetric unit. The data set was limited to $2\theta = 35^{\circ}$. The structure could not be solved for several years. When the solution was finally obtained (by relaxing the centrosymmetric constraint), the reflection/parameter ratio was too low to allow for realistic anisotropic refinement. We no longer have the crystals for collection of a more complete data set. Final values are R = 0.092 and $R_w = 0.091$. Atom positions are shown in Table 3.

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 (24) Sheldrick, G. M. A Program for Crystal Structure Solution;

⁽²⁴⁾ Sheldrick, G. M. A Program for Crystal Structure Solution; Institute für Anorganische Chemie der Universität, Gottingen, FRG.