

heavy atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structures, but their positions were not refined. All calculations, including the full-matrix least-squares refinement, were performed with use of the Enraf-Nonius SDP program package on a VAX computer.

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Supplementary Material Available: Listings of fractional coordinates, anisotropic thermal parameters, and all bond distances and angles (48 pages); listings of observed and calculated structure factors (78 pages). Ordering information is given on any current masthead page.

Synthesis, Structure, Reactivity, and Diastereoisomer Separation of (tropone)Fe(CO)₂L Complexes (L = PPh₃, (+)-Neomenthyldiphenylphosphine)

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The title complexes have been prepared by amine oxide substitution of (tropone)Fe(CO)₃. The solid-state molecular structure of (tropone)Fe(CO)₂PPh₃ reveals a distorted-square-pyramidal geometry with a basal PPh₃ trans to the keto-substituted C=C bond; in solution, both basal isomers are populated. Rates of normal and inverse electron demand cycloaddition, and of sigma-haptotropic rearrangement, are much enhanced relative to those for the tricarbonyl. The (tropone)Fe(CO)₂(+)-neomenthyldiphenylphosphine diastereoisomer of 6*S* planar chirality may be isolated by crystallization. Though the rate of the 1,3-shift is enhanced relative to that for the tricarbonyl, normal and inverse electron demand cycloadditions and electrophilic attack proceed under mild conditions without racemization of the planar chirality.

Introduction

Cyclic and acyclic (η^4 -polyene)Fe(CO)₃ complexes continue to attract attention as intermediates, particularly for asymmetric synthesis.¹ For η^4 -triene complexes such as (tropone)- or (cycloheptatriene)Fe(CO)₃, interest has centered particularly on the regio- and stereoselectivity of reactions at the uncoordinated double bond. Thus, (tropone)Fe(CO)₃ (**1a**) may be protonated² or acylated³ at C-1 and undergoes 1,2-cycloadduct formation with a variety of reagents, including 3,6-bis(methoxycarbonyl)-1,2,4,5-tetrazine,⁴ cyclopentadiene,⁵ nitrile oxides⁶ or imines,⁷ and diazoalkanes.⁸ The last has received application in the synthesis of cyclohexenone⁹ and β -thujaplicin,³ while 1,2-addition of CpFe(CO)₂(η^1 -allyl) complexes to oxygen-alkylated (tropone)Fe(CO)₃ provides access to 4-keto-hydroazulenes.¹⁰ Concerted cycloaddition of tetracyanoethylene (TCNE)¹¹ or 4-phenyltriazoline-3,5-dione (NPT-D)¹² results in kinetically controlled, predominant 1,3-addition; isomerization yields the thermodynamically favored 1,5-cycloadducts, which on oxidative decomplexation yield the product of formal 1,4-addition to the free ligand.¹³

Improved preparations of the related Fe(CO)₂(PR₃) derivatives also make these complexes attractive candidates due to their enhanced reactivity toward electro-

philes,¹⁴ the greater regioselectivity of the reactions of the derived dienyl salts with nucleophiles,¹⁵ and the possibility

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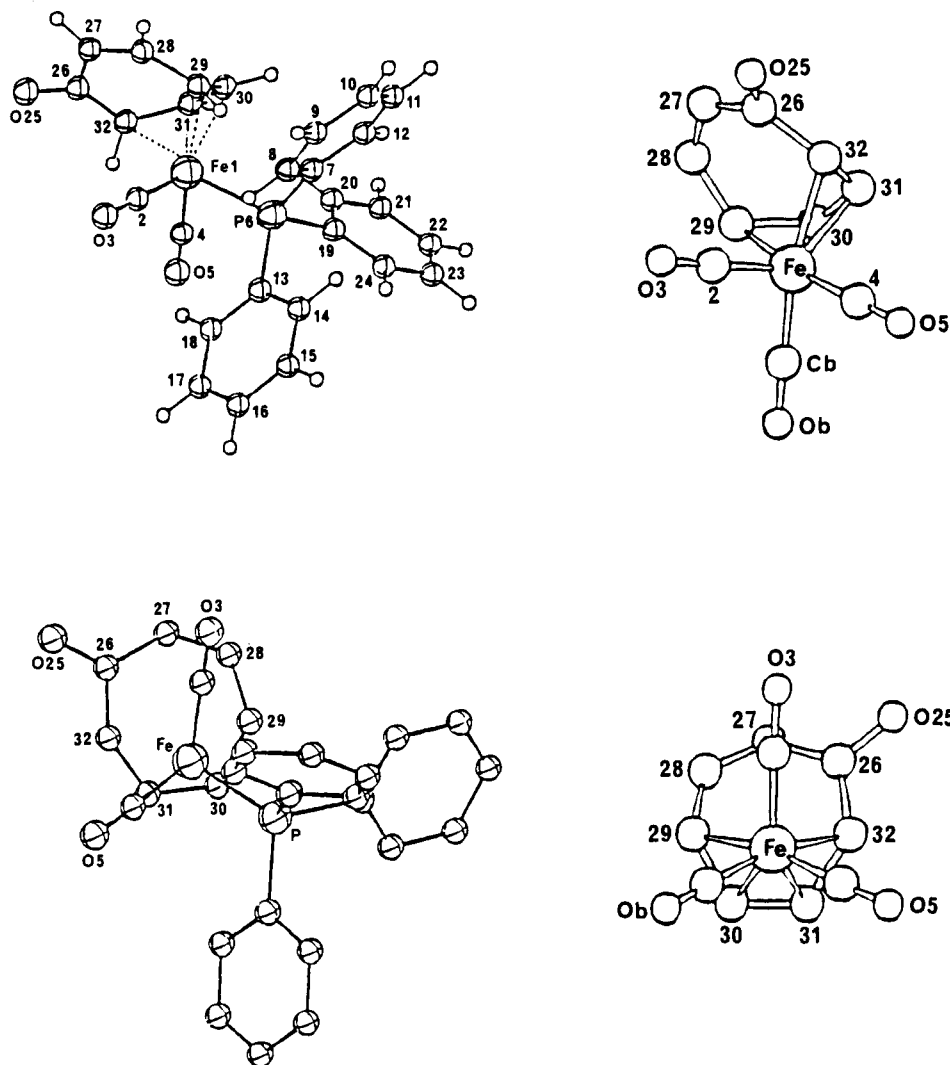


Figure 1. Molecular structures of (right) 1a and (left) 1b.

of using a chiral phosphine as a center of induction¹⁶ or resolution.¹⁷ Here, we describe the changes in reactivity induced by phosphine substitution of 1a, together with full details of the application of (+)-neomenthyldiphenylphosphine (NMDPP) as a resolving center for this chiral complex.

Results

The complexes (C₇H₆O)Fe(CO)₂PPh₃ (1b), (C₇H₆O)Fe(CO)₂P(*m*-C₆H₄Me)₃ (1c), (C₇H₆O)Fe(CO)₂P(*o*-C₆H₄Me)₃ (1d), and (C₇H₆O)Fe(CO)₂((+)-NMDPP) (1e) were prepared by trimethylamine oxide substitution of (C₇H₆O)Fe(CO)₃ (1a).¹⁸

(a) **Solid-State and Solution Structure of 1b.** The solid-state molecular structure of 1b (Figure 1) exhibits the distorted-square-pyramidal structural typical of (diene)Fe(CO)₃ complexes; the phosphine ligand occupies the

basal position trans to the coordinated keto-substituted C=C bond. Table I lists the most important bond lengths and angles, together with the analogous values for 1a.^{19a} At the 3σ level, there are no significant differences in bond lengths. The major structural changes, which are most probably steric in origin, involve a tilting of the diene relative to the Fe-CO_{axial} bond such that the axial CO eclipses C₂₇₋₂₈ rather than C₂₇, coupled with a marked asymmetry in the CO_{axial}-Fe-L_{basal} angles (102.0, 97.3°), which are equivalent (100°) in the tricarbonyl.

Weak nonbonded tropone-PPh₃ interactions are evident in the C_{7,9}-C₂₉ and C_{7,8}-C₃₀ distances of ca. 3.5 Å, an interaction that would be greatly increased in the P(*o*-tolyl)₃ complex 1d (vide infra). Examination of dihedral angles shows little difference in the conformation of the noncoordinated three-carbon fragment; a much more substantial alteration in conformation and decrease in the C₂₆-C₃₂-C₃₁ angle is observed in (1,2,4,6-tetraphenyltropone)Fe(CO)₃^{19b} (numbering as in Scheme I) as a result of minimization of nonbonded interaction between the ketonic CO and neighboring phenyl groups.

Fluxionality in solution is evident in the variable-temperature ³¹P spectra (Figure 2), which show the presence of two populated geometric isomers (1:1.2 ratio in acetone at 225 K, 1:1.6 ratio in dichloromethane at 218 K). The

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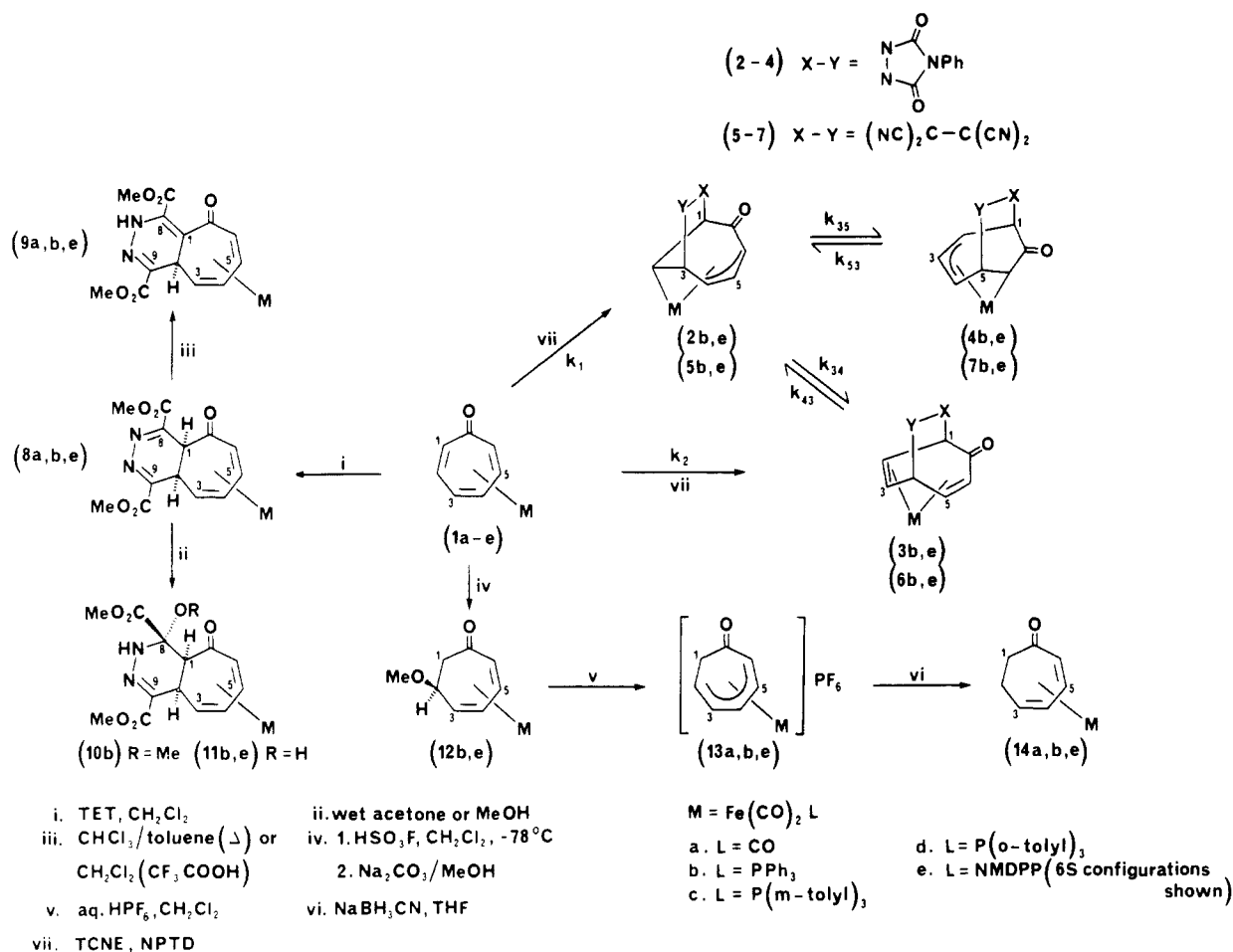
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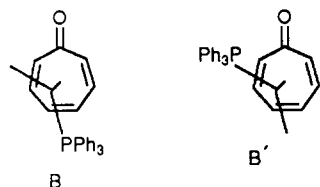
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Scheme I



presence of two phosphorus-coupled resonances assignable to axial carbonyls at 221.0 and 221.3 ppm in the low-temperature ¹³C spectrum (Table II) is consistent with population of the two nonequivalent basal isomers (B/B') of the distorted-square-pyramidal geometry.²⁰



B/B' exchange does not result in complete carbonyl scrambling, and as expected, *two* CO resonances of the correct averaged chemical shift are observed at 293 K, though their broadness precludes measurement of averaged *J*(P-C) values. The absence of the phosphine-substituted axial isomer may be attributed to severe steric interaction of phosphine with the uncoordinated three-carbon fragment (C₇-C₁-C₂).

Separate resonances for the two isomers are also seen at low temperature in the organic ¹³C region and in the ¹H spectrum (Table III, Figure 3). A detailed analysis of the ¹H spectrum reveals that the solid-state conformation B is the *minor* conformer in solution; in particular, the relative upfield shift of H_{3,4} in the minor isomer and H_{5,6} in the major isomer is consistent with shielding by the phenyl rings in B and B', respectively, while the large *J*(P-H_{3,4}) values observed for the minor isomer are consistent with

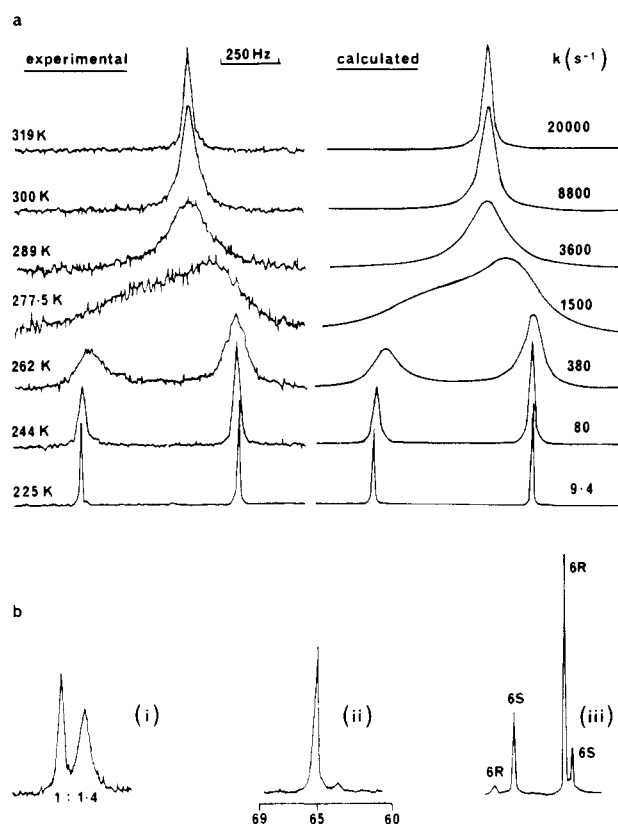


Figure 2. ³¹P NMR spectra of (a) **1b** in acetone-*d*₆ and (b) **1e** in CD₂Cl₂ (i, 6S, 6R equilibrium mixture (273 K); ii, isolated 6S diastereoisomer (273 K); iii, 6S, 6R equilibrium mixture (211 K)).

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Table I. Important Bond Lengths and Angles in 1a and 1b

(a) Bond Lengths (Å)		
	1a	1b
Fe-C ₂	1.757 (9)	1.762 (6)
Fe-C ₄	1.749 (10)	1.776 (7)
Fe-P		2.233 (2)
Fe-C _b ^a	1.771 (10)	
C ₂ -O ₃	1.160 (10)	1.133 (7)
C ₄ -O ₅	1.170 (10)	1.138 (9)
C _b -O _b	1.133 (10)	
Fe-C ₃₂	2.113 (9)	2.129 (8)
Fe-C ₃₁	2.066 (10)	2.039 (6)
Fe-C ₃₀	2.041 (10)	2.037 (2)
Fe-C ₂₉	2.148 (10)	2.135 (8)
C ₂₆ -O ₂₅	1.246 (12)	1.220 (10)
C ₂₆ -C ₃₂	1.493 (13)	1.456 (12)
C ₃₁ -C ₃₂	1.442 (13)	1.443 (9)
C ₃₀ -C ₃₁	1.396 (13)	1.391 (10)
C ₂₉ -C ₃₀	1.436 (14)	1.405 (9)
C ₂₈ -C ₂₉	1.463 (14)	1.469 (14)
C ₂₇ -C ₂₈	1.342 (14)	1.336 (12)
C ₂₆ -C ₂₇	1.447 (14)	1.452 (11)

(b) Bond Angles^b (deg)

	1a	1b
C ₂ -Fe-C ₄	100.4	102.3 (3)
C ₂ -Fe-P		97.3 (3)
C ₂ -Fe-C _b	99.5	
C ₂ -Fe-C ₃₂	95.4	100.6 (3)
C ₂ -Fe-C ₂₉	94.2	90.4 (3)
C ₂ -Fe-C ₃₁	133.1	136.9 (3)
C ₂ -Fe-C ₃₀	132.3	129.2 (3)
C ₄ -Fe-P		88.5 (2)
C ₄ -Fe-C _b	88.8	
C ₄ -Fe-C ₃₂	90.4	88.5 (3)
C ₄ -Fe-C ₃₁	95.5	95.4 (3)
P-Fe-C ₂₉		96.5 (2)
C _b -Fe-C ₂₉	92.1	
P-Fe-C ₃₀		95.8
C _b -Fe-C ₃₀	95.6	
C ₂₆ -C ₃₂ -C ₃₁	127.5	128.6 (7)
C ₃₀ -C ₃₁ -C ₃₂	120.4	120.2 (7)
C ₂₉ -C ₃₀ -C ₃₁	121.4	119.8 (7)
C ₂₈ -C ₂₉ -C ₃₀	122.2	125.1 (8)
C ₂₇ -C ₂₈ -C ₂₉	126.9	127.1 (8)
C ₂₆ -C ₂₇ -C ₂₈	123.8	124.1 (8)
C ₂₇ -C ₂₆ -C ₃₂	122.9	121.5 (7)
O ₂₇ -C ₂₆ -C ₃₂	115.5	118.7 (7)
O ₂₅ -C ₂₆ -C ₂₇	121.3	119.7 (7)
Fe-C ₄ -O ₅	177.1	177.5 (6)
Fe-C ₂ -O ₃	178.3	177.5 (6)
Fe-C _b -O _b	178.1	179.5 (7)

(c) Dihedral Angles

	1a	1b	other ^c
C ₃₀ -C ₃₁ -C ₃₂ -C ₂₆	-49.2	-52.7	-58.5
C ₂₉ -C ₃₀ -C ₃₁ -C ₃₂	4.5	1.8	-2.8
C ₂₈ -C ₂₉ -C ₃₀ -C ₃₁	53.0	52.4	53.2
C ₂₇ -C ₂₈ -C ₂₉ -C ₃₀	-48.2	-43.2	-31.9
C ₂₆ -C ₂₇ -C ₂₈ -C ₂₉	-7.3	-8.9	-5.2
C ₃₂ -C ₂₇ -C ₂₈ -C ₂₉	22.0	14.2	-16.1
C ₃₁ -C ₃₂ -C ₂₆ -C ₂₇	23.2	33.8	66.2

^a C_b-O_b = second basal CO in the tricarbonyl. ^b Standard deviation in angles 0.8–0.9° for 1a. ^c Value for (1,2,4,6-tetraphenyltropone)Fe(CO)₃.

the small P-Fe-C-H_{3,4} dihedral angles in B.

Line-shape analysis of the variable-temperature ³¹P spectra yields a value of ΔG[‡](298 K) = 51 ± 4 kJ mol⁻¹, indistinguishable from the value reported previously for the tricarbonyl.²¹ Both the isomer distribution and free energy of activation are, however, sensitive to phosphine cone angle. Thus, although the analogous P(*m*-tolyl)₃

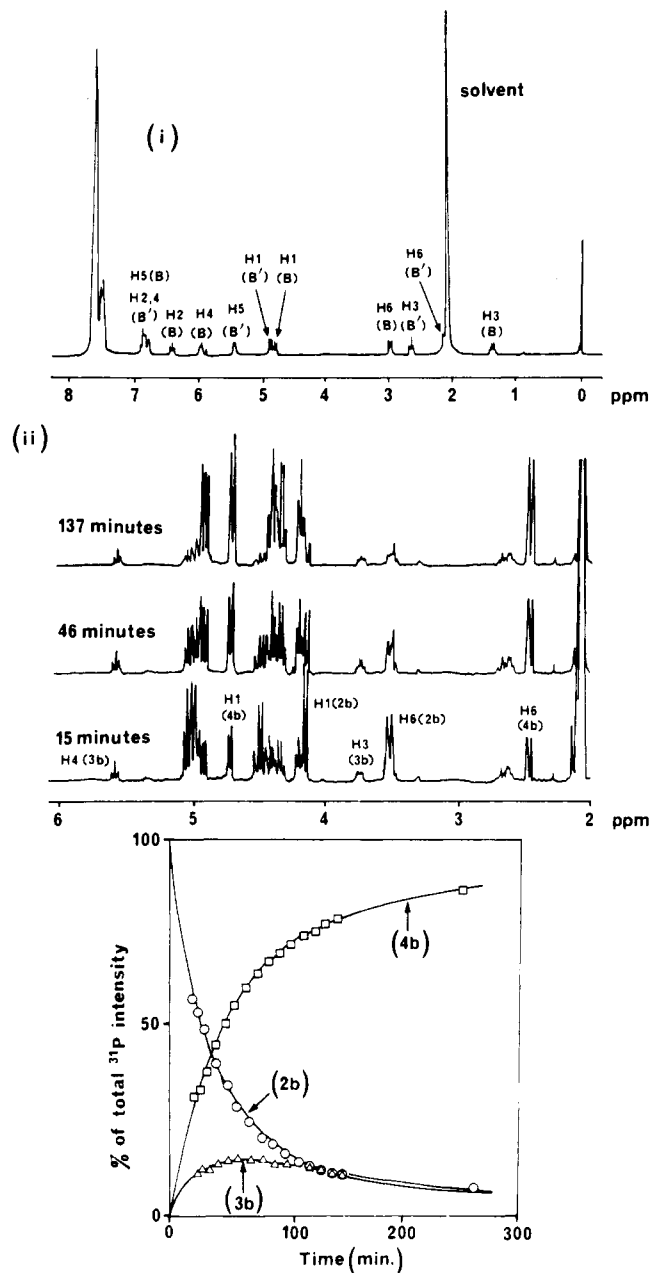


Figure 3. Low-temperature ¹H NMR spectra of 1b and its reaction with NPTD; (i) 1b in acetone-d₆ at 213 K; (ii) 1b + NPTD in acetone-d₆ at 264 K.

complex 1c exhibits behavior very similar to that of 7b (isomer ratio 1:1.8 at 208 K), the P(*o*-tolyl)₃ complex 1d (cone angle 194°) exhibits a limiting low-temperature ³¹P spectrum at only 253 K with an isomer ratio of 1:4.5. Three methyl resonances assignable to the P(*o*-tolyl)₃ ligand may be observed in the ¹H spectrum at 253 K, consistent with a restricted rotation about the Fe-P axis. These resonances broaden and coalesce at a rate similar to that for the coalescence of the B/B' resonances in the ³¹P NMR spectrum, though in neither case can a limiting high-temperature spectrum be obtained before decomposition (ca. 333 K). It is possible that B/B' exchange and Fe-P bond rotation may be synchronous.

These results indicate that the basal position trans to the keto group is sterically the most hindered. All of the η⁴-1,3-diene complexes derived from 1b (Scheme 1) also show two resonances in the limiting low-temperature ³¹P spectra (Table II). With one exception (the tetrazine adduct 8b), B' remains the most populated basal isomer. The

Table II. Spectroscopic Data

complex	IR ^a	NMR				
		¹ H ^b		¹³ C ^c		³¹ P ^d δ
		assignt	δ	assignt	δ	
1a		6	3.0 (m)	4, 5	91.0, 95.7	
		4, 5	5.08 (m)	3, 6	51.8, 59.9	
		3	1.70 (t)	1, 2	120.9, 148.2	
		2	5.72 (m)	7	197.5	
		1	4.94 (dq)	CO	207.5 (br)	
				CO	203.1, 204.3, 213.4 [223 K]	
1b	1995	6	2.99 (t)	4, 5	92.8, 96.3	66.0 (br)
	1939	4	5.50 (t)	3, 6	49.0, 61.0 (br)	64.9, 70.1 [218 K] (1.6:1)
		5	4.93 (m)	1, 2	121.3, 149.9	
		3	1.83 (t)	7	200.1	
		2	6.07 (m)	CO	216.9, 215.1 (br)	
		1	5.18 (dq)	CO	221.3 (7.3), 221.0 (7.4), 209.7 (25.6) [215 K]	
1c	1992	6	2.55 (t, br)	4, 5	93.2, 96.4	63.1 (br)
	1934	4	5.83 (m, br)	3, 6	48.6, 61.2 (br)	62.5, 69.7 [208 K] (1.8:1)
		5	5.30 (m, br)	1, 2	123.0, 150.0	
		3	1.93 (q, br)	7	200.3	
		2	6.36 (m)	CO	217.2, 214.9 (br)	
		1	4.76 (dq)	Me	21.4 (br)	
1d		Me	2.21 (s)			
	1988	6	2.91 (t, br)	4, 5	96.2, 99.4 (br)	52.8 (br)
	1932	4	5.65 (t, br)	3, 6	42.5, 63.1 (br)	51.9, 56.0 [253 K] (4.5:1)
		5	4.22 (m, br)	1, 2	122.5, 150.1 (br)	
		3	1.77 (t)	7	201.4	
		2	6.10 (t, br)	Me	23.2 (br)	
1e ^f		1	5.31 (dq)	Me	21.9 (6.1), 22.9 (3.7) [243 K]	
		Me	1.27 (s)			
			2.40 (s)			
			2.46 (s)			
	1984			4, 5	92.6, 89.9 (br) [283 K]	63.2 (br) (6S)
	1928			3, 6	49.8, 59.0 (br)	62.7, 64.5 [211 K] (1:1.7)
14b ^h				1, 2	121.1, 150.7	
				7	206.8	61.7 (br) (6R)
	1986	1 _{exo}	1.70 (m)	4, 5	90.1, 92.5	64.2
	1930	1 _{endo}	2.75 (t)	3, 6	57.0 (3.0), 56.8	61.0, 73.3 [198 K] (3.0:1)
		2 _{exo}	2.05 (d)	1, 2	36.4, 38.9	
		2 _{endo}	2.15 (dd)	7	209.0	
14e ^{g,i}		3	2.58 (t)	CO	215.7 (18.6)	
		6	2.89 (dd)		217.0 (13.7)	
		4	4.80 (t)			
		5	4.25 (m)			
	1976			4, 5	92.2, 92.9	66.1 (6S)
	1922			3, 6	55.3, 58.2	61.2, 69.4 [198 K] (1:2.2)
13b				1, 2	36.4, 38.9	63.9 (6R)
				7	208.8	
	2054			2, 6	71.5, 80.3	56.8
	2018			3-5	99.9, 100.7, 103.7	56.9, 58.9 [223 K] (1:1)
				1	33.5	-144 (J(P-F) = 710, PF ₆)
				7	191.7	
13e ^f				2, 6	73.9, 80.6	61.5 (6S)
				3-5	99.4, 102.6, 105.6	60.7 (6R)
	2048			1	33.8	
	2010			7	191.0	
				4, 5	89.6, 92.6	65.1
				3, 6	57.3, 57.5	61.8, 70.4 [206 K] (2.9:1)
12b				1	44.1	
	1986			2	83.8	
	1928			OMe	55.4	
				4, 5	91.6, 93.6	67.2 (6S)
				3, 6	55.3, 59.3	62.2, 68.9 [198 K] (1:8.3)
12e ^f				1	44.1	65.1 (6R)
	1984			2	84.1 (3.0)	
	1930			OMe	55.4	
				4, 5	89.7, 91.5	64.0 (br)
				3, 6	47.5, 54.7 (br)	58.7, 67.9 [213 K] (1:1.6)
8b	1998	4, 5	4.69 (m, br)	4, 5	89.7, 91.5	
	1946	6	2.71 (m, br)	3, 6	47.5, 54.7 (br)	
		3	1.84 (m, br)	1	41.3	
		1	2.75 (d, 8.0)	2	45.4	
		2	4.03 (dq)	7	203.3	
		CO ₂ Me	3.69 (s)	CO ₂ Me	53.2, 53.4	
		3.76 (s)	CO ₂ Me	152.9, 154.8		
			8, 9	e		

Table II (Continued)

complex	IR ^a	NMR				
		¹ H ^b		¹³ C ^c		³¹ P ^d δ
		assignt	δ	assignt	δ	
8e^f	1996 1942			4, 5	87.8, 96.2	65.6 (6S)
				3, 6	48.8, 52.2	61.6, 68.8 [203 K] (1:8.8)
				1	40.8 (2)	
				2	44.9	63.3 (6R)
				7	202.8	
				CO ₂ Me	52.6, 53.0	
				CO ₂ Me	152.6, 154.7	
				8, 9	<i>e</i>	
9b	1986 1938	4, 5	5.03 (m)	4, 5	90.3, 92.3	63.7
		6	2.98 (t)	3, 6	55.4, 59.7	60.0, 68.4 [208 K] (1.7:1)
		3	2.65 (m)	2	45.9	
		2	4.90 (s)	7	202.6	
		CO ₂ Me	{ 3.69 (s)	CO ₂ Me	52.4, 52.8	
			{ 3.80 (s)	CO ₂ Me	160.3, 164.3	
		NH	7.69 (br)	1, 8	121.2, 123.0	
				9	<i>e</i>	
9e^f	1984 1930			4, 5	89.9, 95.8	64.9 (6S)
				3, 6	62.9, 53.1 (br)	58.2, 67.0 [203 K] (1:6.9)
				2	46.2 (br)	
				7	203.7	
				CO ₂ Me	52.8	63.3 (6R)
				CO ₂ Me	160.4, 164.1	
				1, 8	121.5, 122.7	
				9	<i>e</i>	
10b	1992 1940	4	4.93 (t, br)	4, 5	89.4, 92.7	62.7
		5	4.53 (m, br)	3, 6	46.8, 55.6	59.4, 67.9 [213 K] (4.4:1)
		6	2.84 (t, br)	1, 2	45.9, 46.8	
		3	1.90 (d, br)	7	203.8	
		1, 2	{ 3.38 (d)	8	85.1	
			{ 3.50 (d) AB (8 Hz)	CO ₂ Me	50.6, 53.2	
		CO ₂ Me	{ 3.70 (s)	CO ₂ Me	163.5, 168.0	
			{ 3.79 (s)	OMe	50.6	
		OMe	3.03 (s)	9	<i>e</i>	
		NH	<i>e</i>			
11b	1992 1938	4	4.98 (t, br)	4, 5	89.7, 92.2	63.6
		5	4.57 (m, br)	3, 6	47.7, 55.4	59.8, 67.7 [213 K] (2.9:1)
		6	2.83 (t)	1, 2	45.4, 48.3	
		3	1.98 (d, br)	7	205.7	
		1, 2	{ 3.42 (d)	8	81.0	
			{ 3.49 (d) AB (7 Hz)	CO ₂ Me	52.1, 53.3	
		CO ₂ Me	{ 3.66 (s)	CO ₂ Me	163.7, 169.3	
			{ 3.77 (s)	9	<i>e</i>	
11e^f	1986 1930			4, 5	89.6, 95.4 (br)	66.7 (6S)
				3, 6	51.0, 51.6 (br)	64.7, 70.6 [223 K] (1:1.3)
				1, 2	44.9, 49.2	
				7	206.4	62.8 (6R)
				8	81.2	
				CO ₂ Me	51.8, 53.1	
				CO ₂ Me	163.7, 169.5	
				9	<i>e</i>	
15	1986 1930	1 _{exo}	1.95 (dd)	3, 4	86.3, 86.6	69.9
		1 _{endo}	2.55 (dd)	2, 5	53.0, 63.0	61.7, 70.1 [193 K] (1:3.0)
		2	2.35 (m)	1	39.6	
		5	3.05 (t)	6	193.3	
		3	4.79 (m)	CO	214.9 (20.8)	
		4	4.68 (m)		216.4 (14.7)	
		CH ₃ CO ₂ Et	{ 3.92 (q)			
			{ 3.92 (s)			
			{ 1.62 (s)			
7b	2022 1974	1	3.34 (dd) ^f			62.0
		6	2.25 (dq)			
		4, 5	3.63 (m)			
		2	3.91 (t)			
		3	4.34 (q)			
7e^f	2014 1966	1	3.20 (dd) ^f			64.4 (6S, 6R)
		6	<i>f</i>			
		4, 5	3.31 (m)			
		2	3.55 (t)			
		3	4.01 (q)			

Table II (Continued)

complex	IR ^a	NMR			
		¹ H ^b		¹³ C ^c	
		assignt	δ	assignt	δ
4b	2012 1960	6	2.48 (t)		62.4
		4	3.86 (m)		
		2, 3	4.20 (m)		
		1, 5	4.48 (m)		
4e^f	2006 1956	6	2.40 (dd)		68.7 (6S)
		3, 4	3.89 (m, br)		
		1, 2, 5	4.61–4.86 (m)		68.5 (6R)

^a In cm⁻¹; CH₂Cl₂ solution. ^b In ppm from TMS; benzene-*d*₆ solution unless stated otherwise. ^c In ppm from TMS; CDCl₃ solution at 298 K unless stated otherwise; *J*(P–C) values (Hz) in parentheses. ^d In ppm from 85% H₃PO₄; CD₂Cl₂ solution at 298 K unless stated otherwise. ^e Under Ph resonance. ^f Acetone-*d*₆ solution. ^g Only ¹H/¹³C resonances of 6S diastereoisomer listed. ^h PPh₃ resonances (ppm): ¹³C, 128–135 (m); ¹H, 6.9–7.6 (m). Other PPh₃ complexes are similar. ⁱ NMDPP resonance ppm (*J*, Hz): ¹³C, 17.6, 20.0, 21.0 (11.7), 23.7, 28.1 (6.8), 28.7, 30.4 (4.0), 30.9 (6.9), 36.9 (22.5), 39.5 (br), 127.3–135.5 (m); ¹H, 0.25 (Me, 6.8), 0.93, 1.20 (CHMe₂, 6.8), 1.5–3.0 (m), 6.9–7.8 (m). Other NMDPP complexes are similar.

Table III. Low-Temperature Spectroscopic Data for **1b** and in Situ Reactions of **1b,e** with TCNE and NPTD^a

complex	H1	H2	H3	H4	H5	H6	³¹ P
1a (acetone, 293 K)	4.94	6.69	2.96		6.67	3.16	
1b (B) (acetone, 213 K)	4.79	6.43	1.34	5.98	6.87	3.00	69.5
	<i>J</i> (5,6) = 8.0, <i>J</i> (4,6) = 1, <i>J</i> (1,6) = 2, <i>J</i> (4,5) = 5, <i>J</i> (3,5) = 0.5, <i>J</i> (3,4) = 7, <i>J</i> (4,P) = 7, <i>J</i> (2,3) = 8, <i>J</i> (1,3) = 0.5, <i>J</i> (3,P) = 8, <i>J</i> (1,2) = 11						
1b (B')	4.88	6.88	2.60	6.80	5.46	2.16	64.2
	<i>J</i> (5,6) = 7.5, <i>J</i> (4,6) = 1, <i>J</i> (1,6) = 1.5, <i>J</i> (4,5) = 4.5, <i>J</i> (3,5) = 1, <i>J</i> (5,P) = 5.5, <i>J</i> (3,4) = 7, <i>J</i> (2,3) = 8, <i>J</i> (1,3) = 0.5, <i>J</i> (1,2) = 11						
2b (acetone, 264 K)	4.15	2.10	5.05	5.00	4.50	3.52	55.2
	<i>J</i> (1,6) = 2, <i>J</i> (1,2) = 8.5, <i>J</i> (5,6) = 9.5, <i>J</i> (4,6) = 2.5, <i>J</i> (4,5) = 6.5, <i>J</i> (3,5) = 1, <i>J</i> (5,P) = 9, <i>J</i> (3,4) = 6, <i>J</i> (2,4) = 1.5, <i>J</i> (2,3) = 9, <i>J</i> (2,P) = 1.5						
3b (acetone, 264 K)	4.97	3.49	3.73	5.59	2.67	2.61	78.5
	<i>J</i> (1,2) = 8, <i>J</i> (5,6) = 8, <i>J</i> (6,P) = 4, <i>J</i> (4,5) = 7.5, <i>J</i> (5,P) = 3, <i>J</i> (3,4) = 7.5, <i>J</i> (2,3) = 6, <i>J</i> (3,P) = 3.5						
4b (acetone, 264 K)	4.72	4.42	4.35	4.20	4.93	2.46	61.3
	<i>J</i> (1,6) = 2.5, <i>J</i> (1,2) = 7.5, <i>J</i> (5,6) = 9.5, <i>J</i> (4,6) = 1, <i>J</i> (4,5) = 6.5, <i>J</i> (3,5) = 1, <i>J</i> (3,4) = 6, <i>J</i> (2,4) = 3, <i>J</i> (2,3) = 7.5, <i>J</i> (3,P) = 7, <i>J</i> (2,P) = 3						
5b (CH ₂ Cl ₂ , 213 K)							54.9
6b (CH ₂ Cl ₂ , 213 K)							76.9
7b (CH ₂ Cl ₂ , 213 K)							62.2
(6S)- 2e (acetone, 273 K)							61.5
(6S)- 2e (acetone, 193 K)							61.2, 62.9 (1:1)
(6R)- 4e (acetone, 273 K)							61.6
(6R)- 4e (acetone, 193 K)							62.0
(6S)- 4e (acetone, 283 K)							69.4
(6S)- 4e (acetone, 193 K)							69.7, 70.3 (4.4:1)
(6R)- 4e (acetone, 273 K)							68.9
(6R)- 4e (acetone, 193 K)							69.2, 70.2 (3:1)
(6S)- 5e (CH ₂ Cl ₂ , 273 K)							57.6
(6S)- 5e (CH ₂ Cl ₂ , 218 K)							57.8
(6R)- 5e (CH ₂ Cl ₂ , 273 K)							57.6
(6R)- 5e (CH ₂ Cl ₂ , 218 K)							57.8
(6S)- 7e (CH ₂ Cl ₂ , 273 K)							64.4
(6S)- 7e (CH ₂ Cl ₂ , 218 K)							64.5, 65.2 (1:1)
(6R)- 7e (CH ₂ Cl ₂ , 273 K)							64.4
(6R)- 7e (CH ₂ Cl ₂ , 218 K)							64.7

^a In ppm with *J* values given in Hz.

relative stability of B/B' is, however, quite sensitive to ring size; thus, (cyclohexadienone)Fe(CO)₂PPh₃ (**15**), containing one less CH₂ group than **14b**, exhibits a considerably enhanced stability of the B isomer.

(b) Cycloaddition Reactions of 1b. The reaction of **1a** with 4-phenyltriazoline-3,5-dione (NPTD) has recently been studied in detail¹² and proceeds (Scheme I) via kinetically controlled 1,3- and 1,4-addition to give **2b** and **3b**, respectively (*k*₁/*k*₂ = 3 at 297 K), followed by ther-

modynamic equilibration of **2b** and **3b** ([2,2]-sigmahaptotropic shift) and of **2b** with the thermodynamically most stable 1,5-adduct **4b** ([3,3]-sigmahaptotropic shift). Cycloaddition of **1b** with NPTD is too fast to measure by NMR spectroscopy at 297 K but may be monitored at 237 K by ³¹P NMR methods (see Experimental Section); the three cycloadducts yield distinct, single resonances down to 193 K (Table III) that are well separated from the two resonances of **1b** at this temperature.

The data clearly show (a) an increased kinetic periselectivity compared to that of **1a** since only the 1,3-adduct is formed initially with **1b** and (b) an acceleration in the rate of cycloaddition by ca. 5×10^2 ($k_1(\mathbf{1a}) = 1.56 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 297 K; $k_1(\mathbf{1b}) = 1.23 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 237 K). Thermodynamic equilibration via sigma-haptotropic shift occurs only at higher temperature (264 K) and may be monitored by ¹H NMR spectroscopy (Table III, Figure 3), which also provides an unambiguous structural identification of the three cycloadducts. Of particular note and utility are the higher field resonances assignable to H₂ and H₆ of **2b** and **4b** and the coordinated diene pair H_{5,6} of **3b**. The four rate constants of Scheme I may be obtained by a computer fitting of the relevant proton integrals to the rate equations

$$\frac{d[\mathbf{3b}]}{dt} = k_{34}[\mathbf{2b}] - k_{43}[\mathbf{3b}]$$

$$\frac{d[\mathbf{4b}]}{dt} = k_{35}[\mathbf{2b}] - k_{53}[\mathbf{4b}]$$

The good correlation is illustrated in Figure 3 and shows that, relative to the tricarbonyl, the rates of both the [2,2]- and [3,3]-sigma-haptotropic shifts are enhanced by approximately 50-fold, though the thermodynamic equilibrium ratio of the cycloadducts is little affected:

	1b (acetone, 264 K)	1a (acetone, 297 K)
k_{35}, s^{-1}	2.8×10^{-4}	2.9×10^{-5}
k_{53}, s^{-1}	1.2×10^{-5}	1.5×10^{-6}
k_{34}, s^{-1}	8.3×10^{-5}	9.8×10^{-6}
k_{43}, s^{-1}	1.3×10^{-4}	2.0×10^{-5}

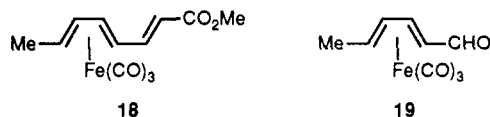
Attempts to measure similar parameters for the cycloaddition and rearrangement in the reaction of **1b** with tetracyanoethylene (TCNE) were frustrated by the extremely fast rate of cycloaddition (complete within mixing time at 223 K) and precipitation of the 1,5-adduct **7b** in the later stages of reaction. Qualitatively, reaction of **1b** with TCNE in CH₂Cl₂ at 223 K yields an 8:1 mixture of **5b** and **6b** that on warming to 253 K isomerizes to an 7:1 equilibrium mixture of **7b** and **5b** with disappearance of the 1,4-adduct **6b**. Comparison with the tricarbonyl^{11a} thus also shows an enhanced rate of sigma-haptotropic rearrangement and a greatly enhanced rate of cycloaddition. The ordering of the rates of cycloaddition (NPTD < TCNE, also observed for **1a**) is usually inverted in most Diels-Alder reactions,²² though hindered dienes such as anthracene are known to react with NPTD more slowly than TCNE.²³

The rate of inverse electron demand cycloaddition of **1b** with 3,6-bis(methoxycarbonyl)-1,2,4,5-tetrazine (TET) is also increased relative to that for the tricarbonyl. Accurate in situ ³¹P NMR monitoring is frustrated by N₂ evolution and the broadness of reactant and product resonances above 243 K, but comparison of an approximate second-order rate constant for the reaction of **1b** with TET in CH₂Cl₂ at 253 K (ca. $10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) with that reported for **1a** in CH₃CN at 307 K ($7.1 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$)⁴ indicates an acceleration of approximately 10^2 . For **1a**, tautomerization occurs under the reaction conditions to yield the 1,4-dihydropyridazine **9a** as the isolated product; this is a general phenomenon, and only in a few cases have the initial 1,5-dihydropyridazine adducts been isolated.²⁴

For **1b**, the acceleration of the cycloaddition allows the isolation of the initial adduct **8b** in good yield. It may be structurally distinguished from **9b** by the two saturated ¹³C resonances and by the strongly coupled H_{1,2} pair ($J = 8 \text{ Hz}$) with H₂ also showing smaller couplings to H_{3,4}. The irreproducibility of the rate of conversion of **8b** to **9b** may be attributed to acid catalysis; tautomerization is complete within minutes upon addition of a trace of CF₃COOH at 293 K. Dipolar 1,2-addition to one C=N bond is evident in the stereo- and regioselective reactions of **8b** with water and methanol to give **10b** and **11b**.²⁵ Though single diastereoisomers are isolated, NMR spectra do not provide an unambiguous assignment; the stereoselectivity shown is based on the folded cis-ring structure evident in the crystal structure of the cycloheptatriene analogue of **9a**,⁴ while the regiochemistry seems most consistent with the observed, known regioselective tautomerization to **9b**.

The increased rates of cycloaddition in both cases are consistent with a frontier molecular orbital approach,^{11a,12,26,27} which shows the primary bonding in (tropone)Fe(CO)₃ to involve the HOMO(tropone)-LUMO(Fe(CO)₃) and LUMO(tropone)-HOMO(Fe(CO)₃) interactions **11** and **17** (Chart I). The former is mainly ligand centered and therefore dominant in orbital-controlled cycloaddition reactions at the organic site. Thus, interaction of **16** with the LUMO of uniparticulate electrophiles is consistent with the predominant 3 + 2 kinetic periselectivity,²⁶ while **16** also possesses the right symmetry for the LUMO(diene)-controlled inverse electron demand 4 + 2 addition of TET. The expected increase in energy of the Fe(CO)₃ valence orbitals on replacement of CO by PR₃ will decrease the tropone-metal interaction in **16**, thus decreasing also the energy separation between **16** and the LUMO of TET, TCNE, and NPTD. Qualitatively, evidence shows that Fe(CO)₃ in (diene)Fe(CO)₃ complexes is a net electron donor,²⁸ an effect which is enhanced by substitution of CO by stronger σ-donors.

A rationale for the influence of phosphine substitution on the rates of the sigma-haptotropic shift is not as obvious, though an orbital analysis of the [3,3]-sigma-haptotropic shift has been published.^{11a} This acceleration of haptotropic exchange is not unique, however, and the rates of 1,3-metal shift in (tropone)Fe(CO)₃ (vide infra) and linear trienes such as **18**, and the racemization of complexes such as **19**, are also accelerated by phosphine substitution.²⁹



(c) **Diastereoisomer Separation and Reactivity of (tropone)Fe(CO)₂(NMDPP).** The planar chirality of (tropone)Fe(CO)₃ was demonstrated for the first time by selective enantiomer photolysis with circularly polarized light.³⁰ Since then, a small-scale separation of enantiomers by HPLC has been achieved,³¹ and subsequent to prelim-

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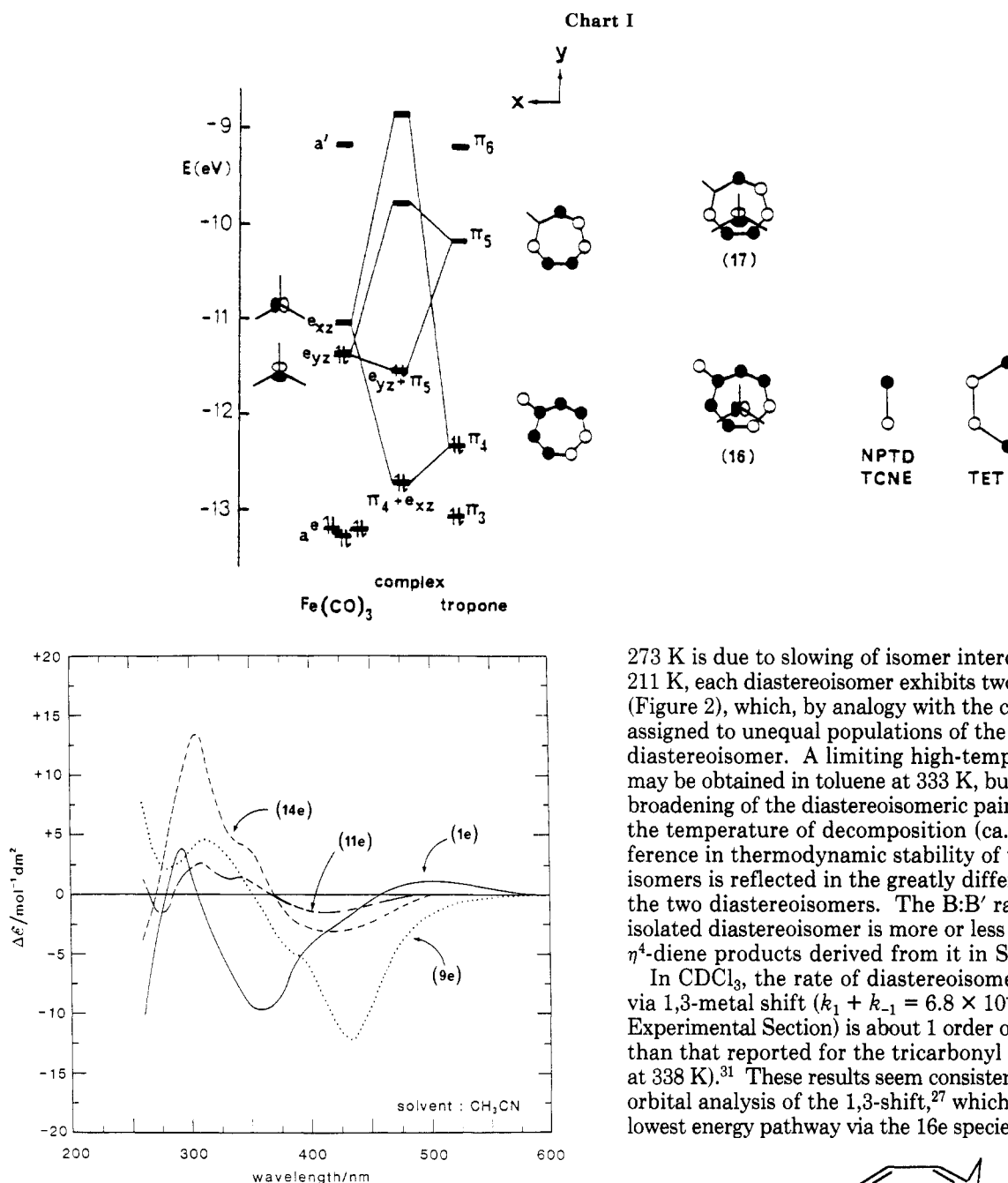


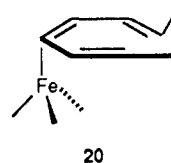
Figure 4. CD spectra of 6S isomers of 1, 9, 11, and 14e.

inary communication of our work,^{17a} a resolution based on attack of chiral nucleophiles on 13a has been reported.³²

Substitution of 1a by NMDPP yields 1e, whose ³¹P NMR spectrum (Figure 2) reveals an unequal population of two diastereoisomers, from which the less abundant isomer may be isolated by crystallization. A single recrystallization reproducibly yields material of 90–95% diastereoisomeric purity, which is suitable for synthetic purposes since the small amounts of second diastereoisomer carried through may be removed by crystallization of reaction products that are not subject to the racemization by the 1,3-shift which occurs in 1e. Diastereoisomer equilibration occurs at room temperature over several hours to yield an equilibrium mixture (1.4:1) which is identical with that obtained from the crude reaction product. Differential broadening of the ³¹P resonances at

273 K is due to slowing of isomer interconversion, and at 211 K, each diastereoisomer exhibits two sharp resonances (Figure 2), which, by analogy with the case for 1b, may be assigned to unequal populations of the B/B' pair of each diastereoisomer. A limiting high-temperature spectrum may be obtained in toluene at 333 K, but no reversible line broadening of the diastereoisomeric pair is observed below the temperature of decomposition (ca. 383 K). The difference in thermodynamic stability of the two diastereoisomers is reflected in the greatly differing B:B' ratios in the two diastereoisomers. The B:B' ratio of 1.7:1 of the isolated diastereoisomer is more or less maintained in the η^4 -diene products derived from it in Scheme I.

In CDCl₃, the rate of diastereoisomer interconversion via 1,3-metal shift ($k_1 + k_{-1} = 6.8 \times 10^{-4} \text{ s}^{-1}$ at 306 K, see Experimental Section) is about 1 order of magnitude faster than that reported for the tricarbonyl ($k = 2.7 \times 10^{-4} \text{ s}^{-1}$ at 338 K).³¹ These results seem consistent with a molecular orbital analysis of the 1,3-shift,²⁷ which shows that in the lowest energy pathway via the 16e species 20 the major loss



of overlap is between the HOMO of tropone and the LUMO of the Fe(CO)₃ fragment. As this stabilization in the η^4 ground state (represented by 16) is expected to be relatively less in 1b as compared to the case for 1a, the barrier to 1,3-shift is correspondingly reduced. In a qualitative way, substitution of CO by phosphine stabilizes the electron-deficient η^2 intermediate.

In structurally similar (diene)Fe(CO)₃ or [(dienyl)Fe(CO)₃]X complexes, the sign of the lowest energy circular dichroism (CD) transition has been proposed as diagnostic of the absolute configuration;^{32,33} spectra of diastereois-

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mers of the type (diene)Fe(CO)₂(NMDPP) are also essentially mirror image in this region and bear a close similarity to the spectrum of the tricarbonyl of the same planar chirality.¹⁷ The strong negative CD absorption at 360 nm shown by the isolated diastereoisomer of **1e** (Figure 4) clearly shows it to have the same planar chirality as (-)-**1a**.³¹ A recent crystallographic determination of the absolute configuration of (+)-**14a**³⁴ thus allows an assignment of 6*S* absolute stereochemistry to the isolated diastereoisomer of **1e** (based on the numbering of Scheme I; designated 2*S* in the numbering scheme of ref 34). All the reactions of (6*S*)-**1e** outlined in Scheme I yield single diastereoisomeric products whose absolute stereochemistry may be assigned as shown on the basis of the known regio- and stereoselectivity of the reactions. Reaction of an equilibrated (6*S*,*R*)-**1e** mixture shows that, in all but one case, the product derived from the 6*R* diastereoisomer may be easily distinguished by ³¹P NMR spectroscopy (Table II). For the η⁴-diene complexes **1e**, **8e**, **9e**, **11e**, and **14e**, broadness and overlap of all but the inner diene resonances with those of the neomenthyl group limit the utility of ¹H NMR spectroscopy in structural assignment; ¹³C spectra are, however, unambiguous and closely resemble those of the PPh₃ complexes. The σ,π-allyl adducts **4b,e** and **7b,e** are too insoluble to permit recording of ¹³C spectra.

Cycloaddition reactions of (6*S*)-**1e** parallel those of **1b**. Reaction with an equimolar amount of TET is complete within 1 h at 253 K to yield the adduct (6*S*)-**8e**, which undergoes acid-catalyzed tautomerization to give (6*S*)-**9e** or hydration to give (6*S*)-**11e**; CD spectra (Figure 4) show clearly the retention of planar chirality during these transformations. Reaction of (6*S*)-**1e** with TCNE in CH₂Cl₂ is complete within mixing time at 228 K to yield predominantly **2e**, which when it is warmed to 253 K isomerizes without racemization to a 7.2:1 equilibrium mixture of **4e** and **2e**. Similarly, reaction of (6*S*)-**1e** with NPTD in acetone is complete within 1 h at 223 K to yield predominantly **5e**, which on warming to 273 K isomerizes without racemization to an 7.1:1 equilibrium mixture of **7e** and **5e**. In neither case can the 1,4-adducts **3e** and **6e** be detected, either as kinetic products or at thermodynamic equilibrium. At room temperature, all of the σ,π-allyl adducts show single ³¹P resonances indicative of a single site occupancy within the pseudooctahedral geometry. Though the ³¹P NMR spectra of the PPh₃ complexes show no temperature dependence, the singlet resonances of several of the NMDPP diastereoisomers show a broadening on cooling and resolution into two resonances at low temperature (Table III). Since site interconversion in the pseudooctahedron does not occur on the NMR time scale,³⁵ the doubled resonances seem most likely associated with inequivalent isomers resulting from restriction of rotation about the Fe-P bond.

Finally, we have examined the possibility of racemization during electrophilic attack (protonation) on **1e**. Protonation of the tricarbonyl at low temperature is known to give initially the hydroxytropylium cation **21a**, which isomerizes to **22a** on warming, with protonation occurring endo at the uncoordinated double bond. Indirect evidence suggests that though racemization via 1,2-shifts is slow in **21a** (*t*_{1/2} ca. 30 min at 313 K), the rate is considerably enhanced by alkyl substitution of **1a** and considerably reduced by PPh₃ substitution of **1a**.³⁶ Protonation of **1b**

Table IV. Atomic Positional and Thermal Parameters of Compound **1b**^a

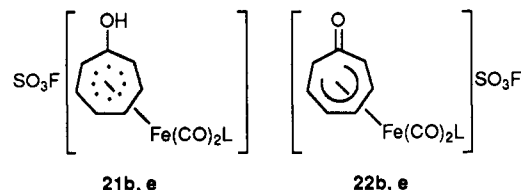
atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} , Å ²
Fe ₁	0.7752 (1)	0.2575 (1)	0.3211 (1)	0.0322 (3)
C ₂	0.7865 (8)	0.1108 (7)	0.4483 (6)	0.0439 (30)
O ₃	0.7927 (7)	0.0165 (5)	0.5304 (4)	0.0776 (27)
C ₄	0.5772 (8)	0.2642 (6)	0.3079 (5)	0.0424 (27)
O ₅	0.4486 (6)	0.2698 (5)	0.3028 (5)	0.0675 (29)
P ₆	0.8467 (2)	0.1685 (1)	0.1915 (1)	0.0318 (6)
C ₇	1.0565 (6)	0.1417 (4)	0.1469 (4)	0.0408 (30)
C ₈	1.1391 (6)	0.2296 (4)	0.0408 (4)	0.0718 (41)
C ₉	1.3021 (6)	0.2121 (4)	0.0115 (4)	0.1019 (62)
C ₁₀	1.3825 (6)	0.1066 (4)	0.0883 (4)	0.0896 (61)
C ₁₁	1.2999 (6)	0.0186 (4)	0.1944 (4)	0.0857 (49)
C ₁₂	1.1369 (6)	0.0362 (4)	0.2236 (4)	0.0669 (41)
C ₁₃	0.7794 (5)	0.0003 (4)	0.2443 (4)	0.0359 (26)
C ₁₄	0.8669 (5)	-0.0909 (4)	0.2030 (4)	0.0701 (41)
C ₁₅	0.8171 (5)	-0.2189 (4)	0.2465 (4)	0.0829 (48)
C ₁₆	0.6798 (5)	-0.2555 (4)	0.3314 (4)	0.0666 (37)
C ₁₇	0.5924 (5)	-0.1643 (4)	0.3728 (4)	0.0550 (32)
C ₁₈	0.6422 (5)	-0.0363 (4)	0.3292 (4)	0.0490 (30)
C ₁₉	0.7816 (6)	0.2589 (3)	0.0510 (4)	0.0407 (27)
C ₂₀	0.7908 (6)	0.2001 (3)	-0.0262 (4)	0.0615 (37)
C ₂₁	0.7490 (6)	0.2743 (3)	-0.1352 (4)	0.0739 (40)
C ₂₂	0.6981 (6)	0.4073 (3)	-0.1669 (4)	0.0603 (36)
C ₂₃	0.6889 (6)	0.4662 (3)	-0.0896 (4)	0.0590 (36)
C ₂₄	0.7307 (6)	0.3920 (3)	0.0193 (4)	0.0495 (31)
C ₂₅	0.6823 (7)	0.3894 (7)	0.5812 (5)	0.0852 (34)
C ₂₆	0.7704 (9)	0.3758 (7)	0.4974 (6)	0.0554 (36)
C ₂₇	0.9361 (10)	0.3407 (8)	0.4997 (7)	0.0641 (42)
C ₂₈	1.0359 (9)	0.3005 (8)	0.4232 (7)	0.0603 (40)
C ₂₉	1.0056 (8)	0.3010 (7)	0.3158 (7)	0.0531 (36)
C ₃₀	0.9274 (9)	0.4052 (7)	0.2347 (6)	0.0537 (34)
C ₃₁	0.7806 (9)	0.4557 (6)	0.2733 (6)	0.0529 (32)
C ₃₂	0.7066 (8)	0.3988 (6)	0.3957 (6)	0.0464 (30)

^a *U*_{eq} is one-third of the trace of the orthogonalized *U*_{ij} tensor. The phenyl substituents were refined and geometrically constrained rigid groups.

Table V

time, s	% of total integrated ³¹ P NMR intens			
	1b	2b	3b	4b
0	100	0	0	0
720	87	12	0.9	0
1330	75	25	0.2	0
1940	72	28	0.3	0
2550	64	36	0.2	0
3160	62	37	0.8	0
3770	61	36	1.2	1.9
4330	60	38	1.0	0.9
5600	57	42	0.9	0.8
6210	56	42	1.1	0.9

or (6*S*)-**1e** with HSO₃F at 195 K yields initially the dark red-brown hydroxytropylium cations **21b,e**, which on



standing for a few minutes isomerize to the light yellow **22b,e**; neutralization with Na₂CO₃/MeOH at low tem-

(34) Sotokawa, H.; Tajiri, A.; Morita, N.; Kabuto, C.; Hatano, M.; Asao, T. *Tetrahedron Lett.* 1987, 28, 5873.

(35) The ¹³C spectrum of the tricarbonyl analogue of **7b** exhibits three CO resonances at room temperature.^{11a}

(36) (a) Eisenstadt, A.; Winstein, S. *Tetrahedron Lett.* 1971, 613. (b) Brookhart, M. S.; Lewis, C. P.; Eisenstadt, A. *J. Organomet. Chem.* 1977, 127, C14. (c) Hunt, D. F.; Farrant, G. C.; Rodeheaver, G. T. *J. Organomet. Chem.* 1972, 38, 349. (d) Eisenstadt, A. *J. Organomet. Chem.* 1975, 97, 443. (e) Lewis, C. P.; Kitching, W.; Eisenstadt, A.; Brookhart, M. *J. Am. Chem. Soc.* 1979, 101, 4896.

(37) Reaction of **13b** with Et₃SiH-CF₃COOH^{36c} results in extensive decomposition, while use of NaBH₄³⁸ yields both **14b** and the σ,π-allyl product resulting from attack at C₃.

(38) Eisenstadt, A. *J. Organomet. Chem.* 1976, 113, 147.

Table VI

complex	mp, °C	anal., %					
		found			calc		
		C	H	N	C	H	N
1b	181–182	67.2	4.36		67.5	4.38	
1c	145–146	68.8	5.24		68.9	5.17	
1d	136–138	68.9	5.31		68.9	5.17	
(6 <i>S</i>)- 1e	156–157	68.6	6.62		68.6	6.46	
15^a	147–149	64.5	5.23		64.8	5.22	
4b	178–181 (dec)	63.9	3.92	6.69	64.1	3.97	6.41
(6 <i>S</i>)- 4e	149–151 (dec)	65.1	5.83	5.93	65.3	5.58	5.86
7b	158–159 (dec)	64.8	3.29	9.21	65.1	3.45	9.21
(6 <i>S</i>)- 7e^b	144–145 (dec)	66.2	5.75	7.59	65.9	5.13	7.69
8b	207–209	60.5	4.16	4.29	60.9	4.15	4.31
9b	225–226	61.2	3.87	4.33	60.9	4.15	4.31
(6 <i>S</i>)- 9e	135–137	62.3	5.47	4.01	62.4	5.76	3.93
10b	184–185	59.6	4.42	4.25	59.8	4.55	4.11
11b	202–204	59.2	4.20	4.05	59.3	4.34	4.19
(6 <i>S</i>)- 11e	157–159	60.9	5.87	3.94	60.8	5.89	3.84
13b	155–157 (dec)	52.0	3.55		51.8	3.51	
(6 <i>S</i>)- 13e	142–143	67.3	4.92		67.2	4.77	
14b	137–139	54.3	5.19		54.1	5.23	
(6 <i>S</i>)- 14e	133–135	68.1	6.96		68.3	6.80	

^a Includes 1 mol of CH₃CO₂Et of solvation. ^b Includes 1 mol of acetone of solvation.

perature yields the methyl ethers **12b,e**, which can be converted to the isolated PF₆[−] salts **13b,e** by treatment with aqueous HPF₆. ³¹P spectra of **12e** and **13e** show clearly no loss of planar chirality during these reactions. Reduction of **13b,e** with NaBH₃CN proceeds smoothly to give **14b,e**.³⁶ The CD spectrum of **14e** (Figure 4) confirms the retention of the 6*S* planar chirality expected for overall addition of H₂ to the uncoordinated double bond of (6*S*)-**1e**.

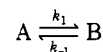
Experimental Section

All reactions were performed with use of distilled, degassed solvents under a nitrogen atmosphere; (tropone)Fe(CO)₃,^{36d} (cyclohexadienone)Fe(CO)₃,³⁹ TET,⁴⁰ and NMDPP⁴¹ were prepared by literature methods. The NMDPP used contained about 10% of phosphine oxide as an impurity. TCNE and NPTD were sublimed before use; FSO₃H was distilled before use. IR spectra were run on a Perkin-Elmer 257 spectrometer and NMR spectra on either a JEOL FX100 or Bruker AM300 spectrometer, the latter equipped with an ASPECT 3000 data system.

(a) Synthesis of (tropone)Fe(CO)₂PPh₃ (1b). (tropone)Fe(CO)₃ (1.4 g, 5.69 mmol) and PPh₃ (2.3 g, 8.78 mmol) were dissolved in acetone (50 mL), and Me₃NO (1.1 g, 9.91 mmol) was added with vigorous stirring. The mixture was refluxed and monitored by infrared spectroscopy and TLC until disappearance of the starting material was essentially complete (ca. 3 h with further periodic addition of more Me₃NO (1.18 g, 10.6 mmol in total)). Diethyl ether (50 mL) was added, and the mixture was filtered through Celite. After removal of solvent, the residue was extracted with 1:1 ethyl acetate–petroleum ether (30–40 °C). After filtration and removal of solvent, the residue was purified by chromatography on alumina with 1:1 ethyl acetate–petroleum ether (30–40 °C) to give, after recrystallization from ethyl acetate–petroleum ether (30–40 °C), (tropone)Fe(CO)₂PPh₃ as red crystals (1.67 g, 61%).

Complexes **1c–e** and **15** were prepared in a similar manner. Unreacted NMDPP was removed from **1e** before chromatography by treatment of a diethyl ether solution of the crude product with MeI. Diastereoisomer separation of **1e** was accomplished by dissolution of 1.5 g of (6*S*)-**1e** in 38 mL of 8:2 ethyl acetate–petroleum ether (30–40 °C) at 65 °C. Crystallization at 5 °C for 48 h yielded 0.18 g of (6*S*)-**1e**.

The rate of diastereoisomer interconversion was measured at 306 K from the ratio of the integrated intensities of the ³¹P NMR resonances of the two diastereoisomers (ρ) as a function of time. For the equilibrium



(where A represents the 6*S* diastereoisomer isolated by crystallization), a plot of $\ln[(\rho_{\infty} - \rho_t)/(\rho_t + 1)] + \ln[(\rho_0 + 1)/(\rho_{\infty} - \rho_0)]$ against time⁴² yields a value of $k_1 + k_{-1} = 6.8 \times 10^{-4} \text{ s}^{-1}$, which for $k_1/k_{-1} = 1.4$ gives $k_1 = 4.0 \times 10^{-4} \text{ s}^{-1}$ and $k_{-1} = 2.8 \times 10^{-4} \text{ s}^{-1}$.

(b) Kinetic Monitoring of Cycloaddition and Isomerization Reactions of 1b with NPTD. Complex **1b** and NPTD were dissolved separately in acetone-*d*₆ and mixed at 195 K to provide a solution 40 mmol dm^{−3} in **1b** and approximately 30 mmol dm^{−3} in NPTD. The reaction was performed with excess **1b** since even freshly sublimed NPTD undergoes some decomposition on standing for short periods; the exact initial concentration of NPTD (20 mmol dm^{−3}) was calculated from the concentration of **1b** remaining after complete reaction.

After placement in the NMR probe at 237 K, the reaction mixture was monitored by using the relative integrations of the ³¹P NMR resonances due to **1b**, **2b**, **3b**, and **4b** (Table V). After conversion to concentrations, a plot of time versus $[1/[A]_0 - [B]_0] \ln\{[A]_t[B]_0/[A]_0[B]_t\}$ (where A and B represent **1b** and NPTD, respectively) yielded k_1 (Scheme I) = $(1.23 \pm 0.18) \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$.

Sigmahaptotropic rearrangements were monitored by dissolution of **1b** and excess NPTD separately in acetone-*d*₆ at 195 K (37 and 40 mmol dm^{−3}, respectively). After the solution was placed in the NMR probe at 264 K, the rearrangement of the initial 1,3-adduct **2b** was monitored by using the relative integration of ¹H NMR resonances; rate constants were evaluated by means of a best-fit computer simulation.

(c) Preparation of NPTD and TCNE Cycloadducts. Complex **1b** (0.25 g, 0.52 mmol) was dissolved in toluene (20 mL) and cooled to 0 °C; NPTD (0.1 g, 0.57 mmol) was added and the mixture stirred for 1 h. After removal of solvent, the product was crystallized from CH₂Cl₂–petroleum ether (30–40 °C) to give **4b** as an off-white powder (0.12 g, 35%). The TCNE adduct **7b** was prepared in a similar way at 25 °C with CH₂Cl₂ as solvent, followed by crystallization from acetone–petroleum ether (30–40 °C). Adducts of (6*S*)-**1e** were prepared in a similar way at 0 °C to minimize racemization.

(d) Preparation and Reactions of Adducts of 1b with TET. (tropone)Fe(CO)₂PPh₃ (0.3 g, 0.63 mmol) was dissolved in CH₂Cl₂ (20 mL) at room temperature; TET (0.124 g, 0.626 mmol) was

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added, and after 20 min of stirring, the solvent was evaporated and the residue crystallized from CH₂Cl₂-petroleum ether (30–40 °C) to give **8b** (0.399 g, 86%) as an orange solid. Addition of 1 drop of CF₃COOH to a dichloromethane solution of **8b**, followed by chromatography on silica gel with ethyl acetate and crystallization from CH₂Cl₂-MeOH, gave **9b** (96%) as a yellow solid. The isomerization may be effected thermally by reflux of a solution of **8b** in 1:1 toluene-CHCl₃ overnight. Crystallization of **8b** from CH₂Cl₂-MeOH yields the methanol adduct **10b** (66%), while the hydrate **11b** may be prepared by reaction of (tropone)Fe(CO)₂PPh₃ (0.2 g, 0.42 mmol) with TET (0.083 g, 0.42 mmol) in 25 mL of 1% water-acetone (acetone previously dried by distillation from MgSO₄) at room temperature for 3 h. Removal of solvent followed by chromatography on Florisil with 1:1 acetone-petroleum ether (30–40 °C) and by crystallization from ethyl acetate-petroleum ether (30–40 °C) gave **11b** (76%) as a yellow solid. Reaction of (6S)-**1e** with TET at 0 °C gave **8e**, characterized spectroscopically. Conversion to **9e** and preparation of **11e** were accomplished as described for **1b**.

(e) Preparation of (cycloheptadienone)Fe(CO)₂PPh₃ (14b). (tropone)Fe(CO)₂PPh₃ (0.35 g, 0.729 mmol) was dissolved in CH₂Cl₂ (60 mL) and cooled to –78 °C; to this was added HSO₃F (1 mL) in CH₂Cl₂ (2 mL) precooled to –78 °C. After several minutes, the dark red-brown color faded to pale yellow and the solution was poured into a suspension of Na₂CO₃ (5 g) in MeOH (10 mL) at –78 °C. After it was warmed to room temperature, the mixture was diluted with water (10 mL) and extracted with CH₂Cl₂ (2 × 35 mL). After being washed with water and saturated NaCl, the extracts were dried (MgSO₄) and evaporated to give **12b** (75%), characterized spectroscopically (Table II). Complex **12b** (0.22 g, 0.43 mmol) was dissolved in CH₂Cl₂ (1 mL) and cooled to 0 °C; with stirring, 75% HPF₆ (0.09 mL) was added, followed after 20 min by diethyl ether (10 mL) to precipitate **13b** (78%), which was filtered and recrystallized from CH₂Cl₂/diethyl ether. Complex **13e** was prepared in the same way.

Complex **13b** (0.85 g, 1.36 mmol) was dissolved in THF (220 mL) and cooled to –78 °C; to this was added NaBH₃CN (0.17 g, 2.71 mmol) in THF (340 mL) precooled to –78 °C. After it was stirred for 15 min, the mixture was warmed to room temperature and stirred for 2 h. After removal of solvent, the residue was dissolved in CH₂Cl₂ (200 mL) and washed with water and saturated NaCl. After drying (MgSO₄) and removal of solvent, the residue was chromatographed on alumina with 1:3 ethyl acetate-petroleum ether (30–40 °C) to give **14b** (55%) as an orange solid, recrystallized from ethyl acetate-petroleum ether (40–60 °C). Complex **14e** was obtained similarly.

(f) Crystal Structure Determination of 1b (C₂₇H₂₁FeO₃P). Diffraction data were measured at ca. 18 °C on an CAD4 diffractometer equipped with a graphite monochromator, using Mo

Kα (λ = 0.71069 Å) radiation. The unit-cell constants were determined by least squares from 25 accurately positioned reflections. The intensities of reflections within 0 < 2θ < 50° ((sin θ)/λ < 0.60 Å^{–1}) were collected by the ω–2θ scan technique with a scan range of (1.0 + 0.3 tan θ)°. All data were recorded at a constant 3° min^{–1} scan rate. Possible deterioration of the analyzed crystals was tested by detecting frequently the intensities of standard reflections and was found to be negligible during the measurements. The data sets were not corrected for absorption or secondary extinction effects.

The compound crystallizes in the triclinic space group *P* $\bar{1}$, with two molecular entities in the unit cell (*Z* = 2). The crystal data are as follows: *M*_r = 480.3; *a* = 8.789 (1), *b* = 11.212 (6), *c* = 12.889 (3) Å; α = 64.43 (2), β = 75.92 (2), γ = 80.98 (2)°; *V* = 1109.4 Å³; *d*_c = 1.438 g cm^{–3}; μ(Mo Kα) = 7.75 cm^{–1}; *F*(000) = 496.

The structure was solved by a combination of direct methods and Fourier techniques (MULTAN80). The refinement was carried out by large-block least squares (SHELX76), including the positional and anisotropic thermal parameters of all the non-hydrogen atoms. The phenyl substituents were treated in the refinement calculations as geometrically constrained rigid groups, to avoid unreliable distortions in their geometry due to the effects of thermal motion. All hydrogens were included in the structure factor computations in calculated positions, the phenyl groups being treated as rigid groups. The final refinements were based only on those observations that satisfied the condition *F*² > 3σ(*F*²), with use of experimental weights (*w* = σ^{–2}(*F*_o)) and minimization of *w*(Δ*F*)². The final difference-fourier maps showed no indication of incorrectly placed or missing atoms, the highest peak and deepest trough not exceeding 0.6 e Å^{–3}. At convergence the discrepancy factors are *R* = 0.057 for 2564 reflections above the intensity threshold (out of 3567 unique data above zero) and a goodness of fit of 1.42 e. The final atomic coordinates of the non-hydrogen atoms are listed in Table IV. Drawings and bond length and bond angle data for **1a** and for (1,2,4,6-tetraphenyltropone)Fe(CO)₃ were generated from the literature atomic coordinates.¹⁹

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Supplementary Material Available: Listings of atomic coordinates of the hydrogen atoms, bond lengths and angles, and anisotropic thermal parameters of the non-hydrogen atoms (4 pages); a table of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.