Protonation of Iron Diene Tris(phosphite) Complexes

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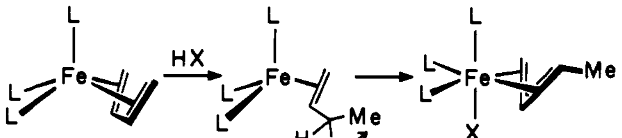
Abstract: The protonation of (η^4-diene)iron (tris(phosphite)) complexes yields (η^3-alkenyl)iron (tris(phosphite)) cations. The noble gas (18-electron) configuration of the iron center is attained through a bonding interaction with a hydrogen atom which is also bound to the carbon atom adjacent to the allylic portion of the π-enyl ligand. The hydrogen atom coordination and resultant distortion of the π-enyl group give rise to unusual ^{1}H NMR parameters. In the π-butenyl complexes, rotation of the methyl group bearing the coordinated hydrogen atom can be frozen out on the NMR time scale. In π-cycloalkenyl complexes, an exchange process, involving the endo hydrogen atoms on the two carbon atoms adjacent to the π-enyl group, can be frozen out on the NMR time scale for cyclohexenyl and cycloheptenyl complexes. The process is still rapid at the lowest temperatures investigated for the cyclooctenyl complex.

Introduction

The protonation of (η^4-diene)iron (L)$_3$ complexes where L is carbonyl has been studied extensively. Early work demonstrated[1] that protonation with coordinating acids, HX, yields **1**. The nature of the species obtained by protonation with noncoordinating acids has been the subject of much subsequent investigation. An initial report[2] of the protonation reaction ascribed a high-field ^{1}H NMR resonance to a metal hydride arising from addition of a proton to the metal center. Such a species has been characterized in a related ruthenium system.[3] The initial work was questioned when a species formulated as the η^3-allyliron tricarbonyl cation[4] was isolated. Further work[5] showed that the species isolated was actually a tetracarbonyl complex with an extra carbonyl arising from partial decomposition of a tricarbonyl intermediate. The high-field proton resonance was rediscovered using a large excess of strong acid.[6] In this case the resonance was assigned to a tetravalent butenyliron hydride formed by diprotonation of the iron precursor, once on the diene and once on the metal. Further work suggested that diprotonation had not occurred,[7,8] but rather that monoprotonation gave a tetravalent hydrido-σ,π-butenyl species, **2a**. Observation of a ^{13}C–^{1}H coupling in a cyclohexenyl complex prompted revision[9] of the bonding to include an additional C–H bond as in **2b**. The model for bonding remained unchanged until recently. Using phosphite rather than carbonyl ligands, we have prepared analogous complexes as isolable species to clearly define the nature of the protonation reaction. Preliminary communications on the preparation[10] and structure[11] of a cyclooctenyl complex have appeared. In this paper we present the preparation and spectroscopic and chemical characterization of the various cyclic and acyclic π-enyl complexes. The X-ray and 30 K neutron diffraction studies of the cyclooctenyl complex will be presented in a subsequent paper.[11b] A detailed picture of the bonding in these cationic species and the unusual neutral paramagnetic species[12] derived by one-electron reduction of the cationic species will also be described.[13]



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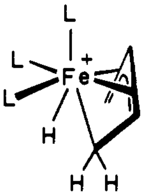
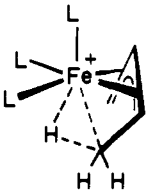
L = CO, X = Cl, Br, CF$_3$CO$_2$



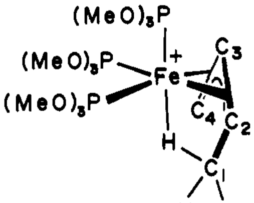
2a



2b

Results

Reaction of Fe(P(OMe)$_3$)$_3$(η^4-butadiene)[14,15] with methanolic acids causes an immediate color change from yellow to orange. The isolated product, **3**, is an octahedral complex with phosphite ligands in three of the coordination sites. The η^3-butenyl group occupies two of the sites and a hydrogen atom on the butenyl methyl group fills the sixth site.



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At room temperature and below, the three phosphorus nuclei show a ^{31}P{^{1}H} NMR spectrum characteristic of an ABC spin system (Table I, Figure 1). As the temperature is raised, the three phosphorus nuclei appear to undergo mutual exchange but decomposition precludes a detailed study of this process.

The ^{1}H NMR spectrum of the butenyl group has several unusual features. The syn and anti protons on C$_4$ are in the expected positions compared to [Fe(P(OMe)$_3$)$_4$(η^3-allyl)]$^+$ [16,17] (see Table II), as is the proton on C$_3$. The syn proton on C$_2$ has a downfield shift as a result of distortions produced by coordination of the hydrogen atom on C$_1$ to the iron center. The observation that, at room temperature, the three hydrogen atoms on C$_1$ occur as a single peak at 5.92 ppm above Me$_4$Si is interpreted as exchange of the coordinated hydrogen atom with the two uncoordinated hydrogen atoms by methyl group rotation. The rotation can be frozen out at −100 °C, where three separate resonances are observed for the methyl protons; the resonance for the hydrogen bridging to the iron atom is 15.2 ppm above Me$_4$Si.

A similar effect of bonding of a hydrogen atom on a saturated carbon to a coordinatively unsaturated metal center was observed in a diethyldi-1-pyrazoylborate molybdenum system[18] and has been studied in detail by Cotton and co-workers.[19-21] The iron and molybdenum systems are both examples

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Table I. $^{31}P\{^1H\}$ NMR Parameters of Alkenyl Tris(phosphite) Complexes

complex	δ,[a] ppm	J[b]	$\Delta H^{\ddagger}$,[c] kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}_{298}$, kcal/mol
$[Fe(P(OMe)_3)_3(butenyl)][BPh_4]$	A 176.4	AB 142			$k_2 > 20$
	B 173.5	AC 46			
	C 164.0	BC 170			
$[Fe(P(OMe)_3)_3(3\text{-methylbutenyl})][BPh_4]$	A 175.5	AB 150			$k_2 > 20$
	B 172.7	AC 34			
	C 162.2	BC 176			
$[Fe(P(OMe)_3)_3(2,3\text{-dimethylbutenyl})][BPh_4]$	A 175.4	AB 140			$k_2 > 20$
	B 172.9	AC 48			
	C 161.1	BC 164			
$[Fe(P(OMe)_3)_3(cyclohexenyl)][BPh_4]$	A 174.9	AB 151	k_1: 10.1	0.2	10.0
	B 174.1	AC 34	k_2: 14.4	−5.1	15.9
	C 165.3	BC 148			
$[Fe(P(OMe)_3)_3(cycloheptenyl)][BPh_4]$	A 175.8	AB 145	k_1: 10.9	1.5	10.5
	B 172.3	AC 35	k_2: 13.9	−9.3	16.7
	C 163.2	BC 160			
$[Fe(P(OMe)_3)_3(cyclooctenyl)][BPh_4]$[d]	A 173.7	AB_2 154			<5 at 123 K
	B_2 168.6		k_2: 16.5	7.4	14.3

[a] In parts per million (positive downfield) from external 85% H_3PO_4. [b] In hertz. [c] k_1 corresponds to the exchange of coordinated hydrogen in the cycloalkenyl species which results in the apparent exchange of A and C leaving B unchanged. k_2 corresponds to the mutual exchange of the three phosphorus ligands. [d] The k_1 process could not be frozen out for the cyclooctenyl complex.

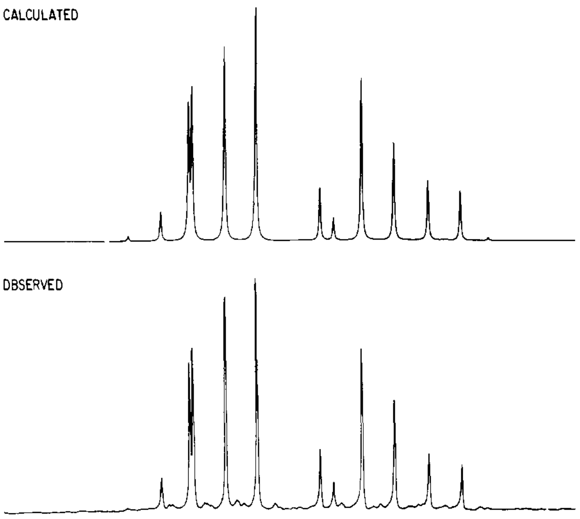
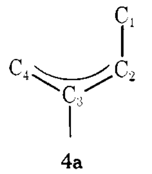


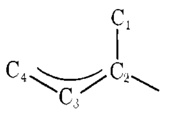
Figure 1. Calculated and observed $^{31}P\{^1H\}$ NMR spectra of $[Fe(P(OMe)_3)_3(\eta_3\text{-butenyl})][BPh_4]$

of coordinatively unsaturated species which achieve coordinative saturation through bonding to an aliphatic hydrogen atom.

The protonation of complexes of the methyl-substituted η^4-dienes, isoprene, and 2,3-dimethylbutadiene gives the related species **4** and **5**. Spectroscopic data for these complexes are reported in Tables I and II. The protonation of dimethylbutadiene can give only one product, but with isoprene there are two possible isomers, **4a** or **4b**. The $^{31}P\{^1H\}$ NMR spectrum



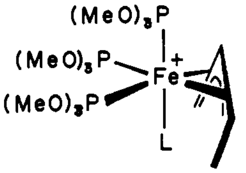
4a



4b

of **4** showed only one product. The ^1H NMR spectrum was equivocal since the chemical shifts of the hydrogen atoms on C_3 and C_2 in the butenyl complex, **3**, are similar. Homonuclear ^1H decoupling experiments established the complex as **4b**.

The isolation of these complexes as tris(phosphite) species is in direct contrast to their carbonyl analogues which were isolated only as tetracarbonyl species. Additionally, $[Fe(P(OMe)_3)_4(\eta^3\text{-allyl})][BPh_4]$ can be prepared[16] by reaction of allyl bromide with $Fe(P(OMe)_3)_5$.[17] It is therefore of interest that the butenyl complexes can be mixed with excess phosphite without formation of the tetraligated species. The steric constraints at the metal center can be investigated by observing the reactions of the butenyl complexes with ligands having smaller cone angles than the phosphite already present.[22] Thus, the butenyl complex **3** reacts with CO or t-BuNC, changing from orange to yellow, and giving **6** and **7**.



L= CO, **6**
t-BuNC, **7**

When the reactions were repeated with the 2,3-dimethylbutenyl complex, **3**, the products isolated were not the simple mono adducts, but instead the bis(phosphite) dicarbonyl and bis(isocyanide) species were formed. To allow coordination of four ligands, the total steric effect had to be reduced slightly by replacing one phosphite with a smaller ligand. This gives a fine distinction between acceptable and unacceptable total steric requirements.

Protonation of tris(phosphite) complexes of cyclic dienes gives complexes which have somewhat different but related spectroscopic properties. The complexes do not have a plane of symmetry since only one of the two endo hydrogen atoms can occupy the sixth coordination site at any given instant, as the structure determination shows.[11] The spectroscopic behavior (Figure 2) of the complex in solution shows that exchange of the two endo hydrogen atoms can be rapid.

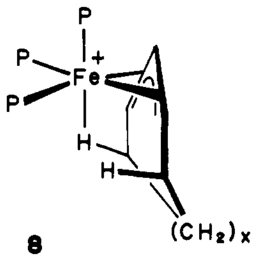


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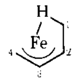
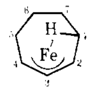
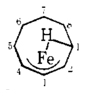
Table II. ^{1}H and ^{13}C{^{1}H} NMR Parameters for π-Alkenyl Iron Cations[a]

complex	nucleus	temp, °C	parameters[b-d]
[Fe(P(OMe)$_3$)$_3$(butenyl)][BPh$_4$]	^{1}H	22	2, 3, 5.60 (1, M), 5.45 (1, M); OMe, 3.77 (9, B), 3.65 (9, B), 3.45 (9, D, J_{PH} = 9); syn 4, 2.54 (1, M); anti 4, −0.14 (1, M); 1, −5.92 (3, M)
	^{1}H	−95	1, −15.2 (1, B), −2.4 (1, B), −2.0 (1, B)
	^{13}C	35	3, 91.9 (1, D, J_{CH} = 165); 2, 67.8 (1, D, J_{CH} = 179), OMe, 53.0 (9, Q, J_{CH} = 147); 4, 39.3 (1, T, J_{CH} = 155); 1, −5.4 (1, Q, J_{CH} = 129)
	^{13}C	−120	1, −3.9 (broad but J_{HC} is ~100 D and 140 T)
[Fe(P(OMe)$_3$)$_3$(3-methylbutenyl)][BPh$_4$]	^{1}H	22	3, 5.22 (1, M); OMe, 3.76 (9, D, J_{PH} = 9), 3.64 (9, D, J_{PH} = 9), 3.42 (9, D, J_{PH} = 10); syn 4, 2.40 (1, M); 2-Me, 2.30 (3, S); anti 4, −0.35 (1, M); 1, −5.94 (3, B)
[Fe(P(OMe)$_3$)$_3$(2,3-dimethylbutenyl)][BPh$_4$]	^{1}H	22	OMe, 3.77 (9, D, J_{PH} = 10), 3.62 (9, D, J_{PH} = 10), 3.45 (9, D, J_{PH} = 10); syn 4, 2.25 (1, M); 2-Me, 3-Me, 2.18 (3, S), 2.07 (3, S); anti 4, −0.39 (1, M); 1, −5.29 (3, M)
	^{1}H	−90	1, −14.8 (1, M), −2.58 (1, M), −2.30 (1, M)
[Fe(P(OMe)$_3$)$_4$(propenyl)][BPh$_4$]	^{1}H	22	3, 4.80 (1, B); OMe, 3.77 (18, D, J_{PH} = 10), 3.70 (9, D, J_{PH} = 10), 3.65 (9, D, J_{PH} = 10); syn 4, 3, 2.62 (2, M); anti 4, 3, 1.81 (2, td, J = 13.7)
[Fe(P(OMe)$_3$)$_3$(cyclohexenyl)][BPh$_4$]	^{1}H	22	(spectrum is exchange broadened) 3, 5.2 (1); syn 4, 2, 4.7 (2); OMe, 3.68 (18), 3.48 (9); 6, exo 1, exo 5, 0.9 (4); endo 1, exo 5, −7.4 (2)
	^{1}H	−70	3, 5.36 (1, M); syn 2, 5.54 (1, M); OMe, 3.76 (18, M), 3.52 (9, M); syn 4, (not observed under OMe); 6, exo 1, exo 5, 1.44–1.06 (4, M); endo 5, 0.58 (1, M); endo 1 −15.75 (1, M)
	^{13}C	35	3, 90.2 (1); 4, 2, 67.1 (2); OMe, 53.6 (9), 6, 19.4 (1); 1, 5, 17.9 (2)
	^{13}C	−80	3, 89.3 (1); 4, 73.7 (1); 2, 60.6 (1); OMe, 53.6 (9), 5, 24.7 (1), 6, 17.2 (1); 1, 13.7 (1)
[Fe(P(OMe)$_3$)$_3$(cycloheptenyl)][BPh$_4$]	^{1}H	22	3, 5.17 (1, M); 4, 2, 4.57 (2, M); OMe, 3.75 (18, B), 2.46 (9, B); ring H 1.4–1.0 (6, B); endo 1, endo 5, −7.14 (2, B)
	^{1}H	−80	2, 5.70 (1, B); 3, 5.20 (1, M); OMe, 3.84 (9, D, J_{PH} = 9), 3.66 (9, D, J_{PH} = 9), 3.46 (9, D, J_{PH} = 10); 4, 3.44 (1, M); ring H, 2.0–0.6 (7, B); endo 1, −15.77 (1, B)
	^{13}C	35	spectrum is broadened: 3, 90 (1); 4, 2, 65 (2); OMe, 53 (9); 7, 6, 21 (2); 1, 5, 15 (2)
	^{13}C	−80	3, 90.7 (1, D, J = 162); 4, 74.5 (1, D, J = 176); OMe, 54–53 (9, Q, J = 147); 2, 52 (maybe, under OMe); 7 or 6, 24.4 (1, T, J = 125) or 18.9 (1, T, J = 125); 5, 21.9 (1, T, J = 125); 1, 7.9 (1, DD, J = 140, 80)
[Fe(P(OMe)$_3$)$_3$(cyclooctenyl)][BPh$_4$]	^{1}H	22	3, 5.54 (1, %, J = 7); 4 and 2, 5.00 (2, Q, t, J = 7); OMe, 3.95 (18, D, J_{PH} = 10), 3.57 (9, D, J_{PH} = 10); ring H, 1.64–1.25 (8, B); endo 1 and endo-5, −6.54 (2, Q)
	^{13}C	35	3, 95.7 (1); 2 and 4, 67.2 (2); OMe, 6 and 8, 27.2 (2); 7, 22.5 (1); 1 and 5, 21.3 (2)
[Fe(P(OMe)$_3$)$_3$(cyclooctenyl-d_1)][BPh$_4$]	^{1}H	22	same as d_0 except slightly broader; peak at −6.5 is of relative integration 1.2; new peak at −7.6 is of relative integration 0.4
	^{13}C	35	3, OMe, and 7 same as d_0 complex; satellite splittings (see text) on three remaining peaks are 2 and 4, 2.3 ppm; 6 and 8, 0.9 ppm; 1 and 5, 6.2 ppm
	^{13}C	−81	same as above except satellite splittings increased: 2 and 4, 4.8 ppm; 6 and 8, 1.6 ppm; 1 and 5, 8.2 ppm
[Fe(P(OMe)$_3$)$_3$(CO)(butenyl)][BPh$_4$]	^{1}H	22	3, 4.75 (1, M); syn 2, 3.94 (1, Q, J = 7); OMe, 3.77 (9, D, J = 4), 3.72 (9, D, J = 4), 3.57 (9, D, J = 10); syn 4, 3.10 (1, t, J = 7); anti 4, 3.11 (1, dd, J = 7, 12); 1, 1.16 (3, dd, J = 3, 7)
[Fe(P(OMe)$_3$)$_3$CO(cyclooctenyl)][BPh$_4$]	^{1}H	22	3, 5.12 (1, M); 4 and 2, 4.09 (2, M); OMe, 3.91 (18, D, J_{PH} = 8), 3.77 (9, D, J_{PH} = 10); endo 1 and 5, 2.36 (2, M); ring H, 1.65–1.35 (8, B)
[Fe(P(OMe)$_3$)$_3$(*t*-BuNC)(cyclooctenyl)][BPh$_4$]	^{1}H	22	3, 4.97 (1, M); 4, 2, 3.72 (2, B); OMe, 3.94 (18, D, J_{PH} = 10); 3.67 (9, D, J_{PH} = 10); endo 1 and endo 5, 2.15 (2, M); ring H, 1.61–1.30 (8, B); *t*-Bu, 1.48 (9, S)

[a] Cations only. Tetraphenylborate is not reported. In CD$_2$Cl$_2$ down to −90 °C. In CD$_2$Cl$_2$/CF$_2$Cl$_2$ below −90 °C. [b] Data presented as atom,[c] chemical shift (integration, pattern,[d] coupling constants[e]). [c] Atom numbering starts at the bridging group and proceeds through the π-enyl group. For N-carbon cycloalkenyl groups, C$_N$ is bonded to C$_1$. [d] Abbreviations are S = singlet, D = doublet, T = triplet, Q = quartet, M = multiplet, B = broad; lower case means resembles a singlet, doublet, triplet, etc. [e] J implies coupling to hydrogen; other couplings are indicated.

At room temperature the ^{1}H NMR spectra of the cyclohexenyl, cycloheptenyl, and cyclooctenyl complexes show resonances around 5.5 and 5.0 ppm (integration 1:2) attributable to the allyl group. There is also a resonance at ~−6.5 ppm (integration 2) attributable to the two endo hydrogen atoms indicated in configuration **8**. The remaining hydrogen atoms are observed in the normal aliphatic region.

When the ^{1}H NMR spectra of the cyclohexenyl and hep-

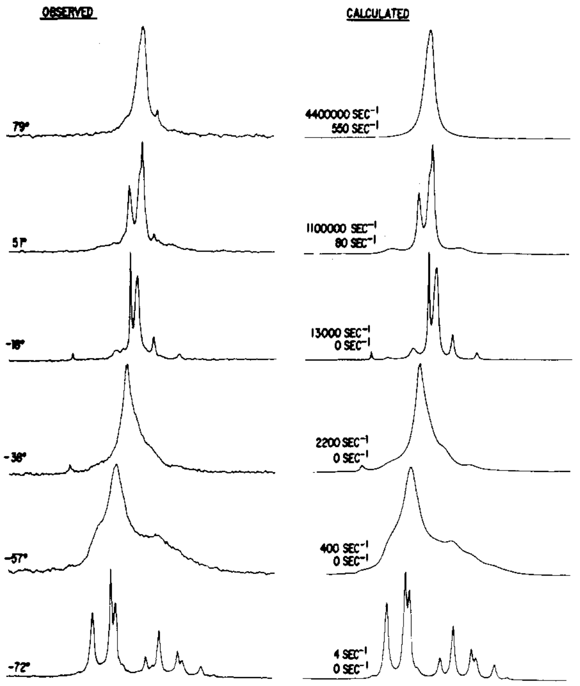
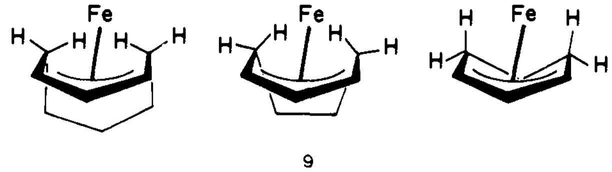


Figure 2. Calculated and observed $^{31}P\{^1H\}$ NMR spectra of $[Fe(P(OMe)_3)_3(\eta_3\text{-cyclohexenyl})][BPh_4]$ as a function of temperature (spin system $ABC \rightarrow AB_2 \rightarrow A_3$).

tenyl complexes are observed at low temperatures (slow exchange), the asymmetry expected from coordination of a single hydrogen atom is observed. The allylic resonance at ~5.5 ppm is unchanged but the higher field allylic resonance is split into two peaks. The peak to high field of Me_4Si is also split; the resonance attributable to the hydrogen bonded to the metal is shifted upfield (~−15 ppm) while the exchange partner is shifted into the normal aliphatic region.

The exchange barrier for the two endo hydrogen atoms is a strong function of the ring size. In the initial study of the cyclooctenyl complex,[10] the exchange process could not be slowed on the NMR time scale even at −150 °C, implying a barrier to exchange of less than 5 kcal/mol. The barriers for the six- and seven-membered rings (obtained from $^{31}P[^1H]$ simulations; vide infra) are 10.0 and 10.4 kcal/mol, respectively. This dependence is attributed to changes in the relative positions of the two exchanging hydrogen atoms as the ring size changes. The positions of five of the carbon atoms of the enyl group are constrained by the enyl bonding. When viewed from the top of the complex (as in configuration **9**) it can be seen that



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reducing the ring size increases the distance between the two endo hydrogen atoms (primarily a torsional deformation). During the exchange process, one hydrogen atom is presumably approaching the metal center as the other is leaving. Because of the larger H–H separation, the smaller ring systems require more complete M–H bond breaking before the new M–H bond making can begin. This provides a rationalization for the increase in activation energy with decreasing ring size. The cyclooctenyl complex provides a new kind of example of the proximity effects characteristic of cyclooctenyl derivatives.[23]

The exchange of the endo hydrogen atoms is best studied via the $^{31}P\{^1H\}$ NMR spectra. When the exchange process is slow, the $^{31}P\{^1H\}$ NMR spectra show ABC splitting patterns since the two equatorial phosphite ligands are nonequivalent (Table I, Figure 2). At temperatures where the two endo hydrogen atoms are under fast exchange conditions, the $^{31}P\{^1H\}$ NMR spectra correspond to tightly coupled AB_2 spin systems. As the temperature is raised still further, the three phosphorus nuclei begin to exchange resulting in a single line (A_3 spin system).

Experimental and simulated $^{31}P\{^1H\}$ NMR spectra for the cyclohexenyl complex are shown in Figure 2. The low-temperature hydrogen exchange process, with rate constant k_1, was simulated at several temperatures below 0 °C. The activation parameters obtained in this way were used in the determination of the rate constants for the mutual exchange of all three phosphorus ligands at higher temperatures.

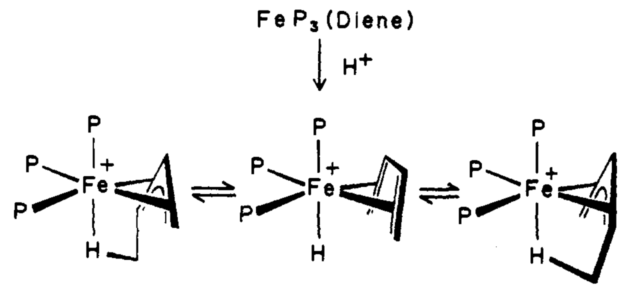
There is no detailed mechanistic information in the higher temperature spectra because the spin system is too simple. Thus, we were unable to distinguish between the two most probable k_2 processes: (a) pairwise axial-equatorial exchange or (b) a Bailar twist mechanism.[24,25] The face rotation pathway of the Bailar twist is attractive by virtue of its resemblance to the turnstile/olefin rotation mechanism which has been established as the mechanism[14,15] for exchange in the iron-(diene) tris(phosphite) precursors, particularly since the complexes considered here are best described as six coordinate. The $^{13}C\{^1H\}$ NMR spectra of the cycloenyl complexes (Table II) are also consistent with the above structures and mechanisms.

As with the butenyl complexes, the hydrogen atom coordination in the cycloalkenyl complexes is readily reversed by addition of ligands with small cone angles. Trimethyl phosphite does not displace the hydrogen atom even when present in large excess, but CO and *t*-BuNC coordinate readily to give complexes analogous to mixed $[FeL_4(enyl)]^+$ species isolated by others.

Deuteration Studies

The tris(phosphite)iron diene complexes are readily deuterated in methanol-d_1 with DCl or DSO_3F to give complexes analogous to those obtained upon protonation. Deuteration of the butadiene complex gives a monodeuterio species; there is no further incorporation of deuterium. Field desorption mass spectrometry[26] indicated about 95% d_1 incorporation. The incorporation produces an unusual effect in the ^1H NMR spectrum. In fast exchange, the original high-field peak is greatly reduced in intensity (not eliminated) and a new resonance, shifted over 1 ppm further upfield, is observed. The new higher field peak arises from the monodeuterated methyl group; the shift is the result of an isotopic dependence of the equilibrium constant for hydrogen and deuterium distribution among bridging and nonbridging positions. Similar results have been observed in some organic systems[27] and more recently by Shapley[28] in a methylated metal cluster system. Because of differences in the zero-point energies of bridging Fe–H–C and nonbridging H–C vibrations, deuterium preferentially occupies a nonbridging site. The two hydrogen atoms are not statistically distributed between the three possible positions, but spend relatively more time in the position bonded to the iron atom. Thus the observed position of the averaged resonance for the two hydrogen atoms is to higher field than would be calculated on a simple statistical basis. ^2H NMR shows a peak shifted downfield from the nondeuterated position, as expected. The ^2H NMR spectra also provide an explanation for the residual peak left at the unshifted position: deuterium resonances are observed for the syn and anti positions on C_4 but not for the positions on C_3 or C_2 (configuration **3**). The single deuterium atom is distributed among five possible positions on the two ends of the butenyl group; when the deuterium is on C_4, the

Scheme I



methyl resonance is unshifted, giving rise to the residual proton peak.

This distribution for the deuterium can be explained by the two-step mechanism of Scheme I. Deuteration (or protonation) of the diene complex is an irreversible process, thus limiting deuterium uptake to one. The deuteride is then transferred to either end of the diene. Rotation of the resultant methyl group followed by reversal of the process will scramble the five terminal positions.

Deuteration of the cyclooctadiene complexes provides additional information about the mechanisms of protonation and hydrogen transfer. Deuterium incorporation takes place entirely in the endo positions relative to the metal. As in the case of the butenyl complex, a portion of the resonance to high field of Me_4Si is shifted further upfield (when observed in fast exchange). The intensity of the unshifted portion is approximately three times that of the shifted portion. Again the ^2H NMR spectrum provides an explanation for these observations. The single deuterium is statistically distributed among the five endo positions on the cyclooctenyl ring. Three-fifths of the time the deuterium is in positions where it cannot interact with the metal, positions which would give rise to normal high-field proton signals. The remaining two fifths of the time the deuterium is on a carbon atom adjacent to the allylic group and can coordinate to the metal. For the same reason as given for the butenyl complex, the distribution between coordinated and noncoordinated deuterium is not statistical, giving rise to an upfield shift of the proton resonance from the expected position and a corresponding downfield shift of the deuterium resonance.

These facts can be used to interpret the observed 3:1 intensity ratio between the unshifted high-field peak and the extra high-field peak which appears on deuteration. Deuterium in positions 6, 7, or 8 (see the numbering scheme in Table II or Figure 3) gives an unshifted upfield peak for the hydrogens at positions 1 and 5. The relative intensity contribution to the unshifted peak is therefore $3 \times 2 = 6$. Deuterium in positions 1 or 5 gives a shifted peak for the remaining hydrogen at position 5 or 1. The relative intensity contribution to the shifted peak is therefore $2 \times 1 = 2$. Thus, the intensity ratio for the two upfield peaks is calculated to be 3:1, in agreement with observation.

The exclusively endo distribution of deuterium in the cyclooctenyl-d_1 complex supports the notion of an intermediate hydridodiene complex. Once the diene complex is deuterated, a mechanism such as Scheme I, in which all reactions occur endo with respect to the metal, does not allow transfer to exo positions on the ring. The three hydrogen atoms on the enyl group and the four hydrogen atoms on the η^4-diene are all "exo" in that they are never involved in hydrogen or deuterium transfer to or from the metal.

The complex ^1H-^1H couplings preclude a detailed analysis of the other ring-proton resonances. The ^{13}C NMR spectra, on the other hand, are readily interpreted (Table II). In fast exchange the cyclooctenyl complex shows five $^{13}C\{^1H\}$ resonances in the ratio of 1:2:2:2:1. If the exchange of the two endo hydrogen atoms on C_1 and C_5 (see Table II or Figure 3 for number scheme) could be frozen out on the NMR time scale, each of the three ^{13}C NMR peaks of relative intensity 2 would be split into two peaks. When the complex is monodeuterated the three averaged resonances develop "satellite" peaks. The unshifted center portions of each of the three resonances correspond to deuterium on C_6, C_7, or C_8 where it cannot interact with the metal center and cause a shift in the bridging-nonbridging equilibrium. The satellite peaks correspond to deuterium on C_1 or C_5. Owing to the nonstatistical distribution of hydrogen and deuterium in the bridging position, the averaged ^{13}C resonances on the deuterium side of the ring are weighted in favor of their nonbridging chemical shifts and the averaged ^{13}C resonances on the hydrogen side of the ring are weighted in favor of their bridging chemical shifts. Thus, the fast exchange average resonance of C_1 and C_5 is split into two weighted average resonances, with the chemical shift of the carbon bearing deuterium shifted downfield toward the slow exchange chemical shift of C_5 and the chemical shift of the carbon bearing the hydrogen atom shifted an equal distance upfield. The shifts are largest for the carbon atoms bearing the interacting hydrogen atoms. The magnitudes of the shifts are very temperature dependent.

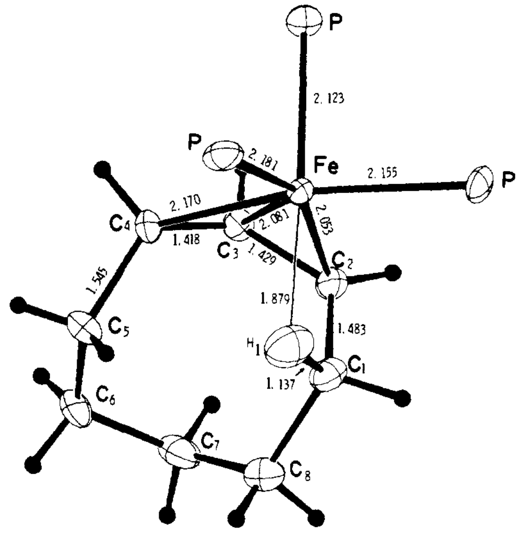


Figure 3. Important aspects of the structure of the $[Fe(P(OMe)_3)_3(\eta^3\text{-cyclooctenyl})]$ cation as determined by neutron diffraction at 110 K (ref 11).

The $^{13}C\{^1H\}$ NMR spectrum of the cycloheptenyl complex was obtained in slow exchange, and seven separate resonances were assigned. Gated decoupling experiments showed that $^1J_{C-H}$ for the bridging hydrogen atom is only 80 Hz while for the other hydrogen atom on the same carbon $^1J_{C-H}$ is 140 Hz. The much smaller $^1J_{C-H}$ for the bridging hydrogen atom suggests considerable weakening of the C–H bond, on the basis of a bonding model which will be discussed in the following section. $^{31}P\{^1H\}$ gated decoupling NMR experiments showed, in general, no coupling between phosphorus and the high-field hydrogen atom. The only possible exception was for the cycloheptenyl complex, where a coupling of less than 1 Hz *may* have been observed. For a conventional iron hydride system, couplings between 10 and 70 Hz would be expected.[29]

Conclusions

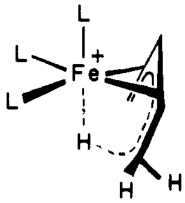
The protonation of dienes which are η^4 coordinated to FeL_3 fragments proceeds through a hydridoiron intermediate to give an η^3-enyl complex in which the hydrogen transfer has taken place endo with respect to the metal. The protonation of noncoordinated dienes normally requires very strong acid systems such as H_2SO_4 or HSO_3F ($pK_a < -10$). This reaction is

Table III. Analyses, Melting Points, and Field Desorption Mass Spectra of Iron π-Enyl Complexes

complex	C, %	H, %	P, %	mp, °C	FDMS
$[Fe(P(OMe)_3)_3(butenyl)][BPh_4]$	55.4	6.78	11.5	189	
	55.2	6.72	11.5		
$[Fe(P(OMe)_3)_3(3\text{-methylbutenyl})][BPh_4]$	56.0	6.80	11.2	187	
	55.8	6.83	11.4		
$[Fe(P(OMe)_3)_3(2,3\text{-dimethylbutenyl})][BPh_4]$	56.4	7.04	11.1	192	
	56.4	7.12	10.9		
$[Fe(P(OMe)_3)_3(cyclohexenyl)][BPh_4]$	56.4	7.04	11.2	203	509
	56.7	6.84	11.2		509
$[Fe(P(OMe)_3)_3(cycloheptenyl)][BPh_4]$	57.0	6.94	11.0	183	
	57.1	6.80	11.3		
$[Fe(P(OMe)_3)_3(cycloheptenyl)][BF_4]$	31.5	6.28	15.2	161	523
	30.6	5.92	14.5		523
$[Fe(P(OMe)_3)_3(cyclooctenyl)][BPh_4]$	57.5	7.06	10.9	130	
	57.5	6.92	11.4		
$[Fe(P(OMe)_3)_3(cyclooctenyl)][BF_4]$	32.7	6.46	14.9	141	537
	32.4	6.36	14.2		537

greatly modified by coordination to the FeL_3 function; the organic moiety is now considered to be anionic rather than cationic[30,31] (with a concomitant oxidation of the metal center). Typically the protonation of $Fe(CO)_3$(diene) complexes is carried out with tetrafluoroboric acid in trifluoroacetic anhydride ($pK_a \approx -6$). It is now evident that the ease of protonation is very dependent on the nature of the ligands, L. When L = $P(OMe)_3$, the relatively weak acid NH_4BF_4 (in methanol, $pK_a = 9$) can be employed. When L = PMe_3,[32] the complex is readily[33] protonated by acids as weak as methanol itself ($pK_a = 16$). Thus the ligand donor-acceptor properties have a strong influence on the basicity of the complex as a whole.

The η^3-enyl complex generated by protonation is nominally a 16-electron system. It achieves an 18-electron configuration through bonding to a hydrogen atom on a carbon atom adjacent to the enyl group. Based upon the structural results[11] and the spectroscopic results given here, the bonding can be pictured as in **10**, implying an open two-electron three-center (2e-3c) bond. The electron density is concentrated in the C-H bonding region, the Fe-H bond being of secondary importance.



10

This view of electron donation by the aliphatic hydrogen atom is supported by the effects of changing the other ligands on the metal center. As electron density on the metal center is increased by introducing more basic ligands, the two electrons become more localized in the C-H part of the three-center bond. Two consequences of this electron-density shift are seen in the changes in the barrier to methyl-group rotation and the changes in $^{13}C-^{1}H$ coupling constants. We assume that the barrier to methyl-group rotation reflects the strength of the Fe-H interaction. As L is changed from CO to $P(OMe)_3$ to PMe_3 the barrier to rotation decreases from 10.2[34] to 8.8 to 8.5 kcal/mol, suggesting a weakening of the Fe-H bond. The The $^{13}C-^{1}H$ coupling constants are expected to increase as the strength of the C-H interaction increases. It is therefore consistent that J_{C-H} increases from 74 Hz[34,35] for the tricarbonyl to 84 Hz for the dicarbonyl monophosphite analogue[34] to ~100 Hz for the tris(phosphite) complex. We were not able to detect a unique C-H coupling in the PMe_3 complex, suggesting that the coupling constants for all three hydrogen atoms on the methyl group in the enyl ligand are approximately equivalent at ~120 Hz. This last observation points out another trend which supports the proposed model for bonding. The $^{13}C-^{1}H$ coupling of the two noncoordinated hydrogen atoms on C_1 is an indication of the hybridization of C_1. In the tricarbonyl complex, the couplings are 147 Hz. They drop to ~140 Hz in the tris(phosphite) complex and ~120 Hz in the tris(phosphine) complex. This trend indicates that the methyl group has considerable sp^2 character in the tricarbonyl complex, but as electron density on the iron is increased it becomes a more normal sp^3 methyl group.

Finally, we note that single-electron reduction of the complexes yields stable paramagnetic species which have been studied spectroscopically over a wide range of temperatures.[12] Evidence for a weak Fe-H interaction was found but no abnormalities in the C-H bonds in the organic fragment were established.[13]

Experimental Section

All reactions were carried out in the nitrogen atmosphere of a Vacuum Atmospheres drybox. All solvents were dried and degassed by standard techniques prior to use. ^1H NMR spectra were obtained in the CW mode, in 5-mm tubes, on a Varian HRSG-IX-VFT 220/300 or a Varian XL-100 spectrometer, the latter for hetero $^1H\{^{31}P\}$ and homonuclear decoupling experiments and variable-temperature work. ^1H chemical shifts, δ, are in parts per million (positive downfield) from internal tetramethylsilane (Me_4Si). $^{31}P\{^1H\}$ NMR spectra were recorded in the FT mode using 10-mm tubes on a Bruker HFX-90 spectrometer equipped with a Digilab FTS/NMR-3 data system. Deuterated solvents were used to provide an internal ^2H lock. ^{31}P chemical shifts are in parts per million (positive downfield) from external 85% H_3PO_4. $^{13}C\{^1H\}$ and ^{13}C NMR spectra were recorded in the FT mode using 10-mm tubes on a Bruker WH-90.[2] $^2H\{^1H\}$ NMR spectra were recorded in the FT mode using 10-mm tubes on a Varian FT-80A at 12.211 MHz.

Infrared spectra were recorded on a Perkin-Elmer 221 spectrometer calibrated with CO gas. Mass spectra were recorded for the complex cations by the field desorption technique on a CEC 21-110B mass spectrometer.[26] Analyses were performed in our own microanalytical facilities. Melting points are uncorrected.

The preparation of the iron η^4-diene tris(phosphite) precursors by metal-atom evaporation was described.[13] Spectroscopic parameters are listed in Tables I and II. Physical characterization parameters for the complexes are listed in Table III.

Preparation of $[Fe(P(OMe)_3)_3(\eta^3\text{-butenyl})][BPh_4]$. A solution of $Fe(P(OMe)_3)_3(\eta^4$-butadiene) (1.45 g, 3.0 mmol) in methanol (30 mL) was reacted slowly with a solution of tetrafluoroboric acid in methanol (1.0 M, 3.0 mL, 3.0 mmol). The yellow solution darkened. The solution was then filtered through Celite to remove a trace of suspended iron metal. A solution of $NaBPh_4$ (1.02 g, 3.0 mmol) in methanol (20 mL) was added slowly, precipitating a yellow, crystalline product. The product was collected by vacuum filtration, washed with ether, and dried under vacuum.

The product was recrystallized by dissolving in CH_2Cl_2, adding methanol until the solution became turbid, and then removing some solvent under vacuum. The resultant loss of CH_2Cl_2 and the effect of the ([illegible] cipitated large, plate-like crystals. The other tris(trimet [illegible] ite) complexes were prepared analogously.

Alte [illegible] ds for Protonation of Fe(P(OMe)$_3$)$_3$(η^4-butadiene). A solution of Fe(P(OMe)$_3$)$_3$(η^3-butadiene) (96 mg, 0.2 mmol) in methanol (1.8 mL) was reacted with 0.4 mmol of each of a series of acids in an NMR tube. The $^{31}P\{^1H\}$ NMR spectra of these mixtures were recorded at −80 °C after at least 1 h. Acids which effected protonation were HCl, 2,4-pentanedione, hexafluoro-2,4-pentanedione, malononitrile, phenol, and NH_4BF_4. Methanol solvent did not protonate the complex.

Attempted Protonation of Fe(P(O-*i*-Pr)$_3$)$_3$(η^4-cyclooctadiene). A. In *i*-PrOH. The protonation was attempted as in the first preparation. No product could be isolated and the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture indicated decomposition of the starting material and Arbuzoff rearrangement of the phosphites.

B. In MeOH. The procedure was repeated in methanol but addition of the methanolic HBF_4 and methanolic $NaBPh_4$ was done rapidly in an attempt to minimize transesterification of the phosphites. Product precipitated for about 1 min. The isolated product was relatively pure tris(trimethyl phosphite)iron cyclooctenyl cation.

Deuteration of Fe(P(OMe)$_3$)$_3$(η^4-diene) Complexes. All reactions were carried out in methanol-d_1. Solutions of 1 M DCl were generated by adding acetyl chloride to methanol-d_1. Alternatively, solutions of 1 M DSO_3F were prepared with commercially available materials. The reactions were carried out like the protonation reactions, but on a 1-mmol scale. Reactions with intervals of 1 min to 2 h between addition of the acid and the Na[BPh_4] showed no apparent difference.

Preparation of [Fe(P(OMe)$_3$)$_3$(*t*-BuNC)(η^3-butenyl)][BPh$_4$]. A solution of [Fe(P(OMe)$_3$)$_3$(η^3-butenyl)][BPh_4] (0.79 g, 1 mmol) in CH_2Cl_2 (20 mL) was treated with a slight excess of *t*-BuNC (0.10 g, 1.2 mmol). The solution lightened over 15 min from orange to yellow. Methanol (15 mL) was added. As the solvent was reduced in volume under vacuum, a pale yellow product precipitated as large, plate-like crystals. The product was collected by vacuum filtration, washed with ether, and dried under vacuum.

Attempted Preparation of [Fe(P(OMe)$_3$)$_3$(*t*-BuNC)(η^3-2,3-dimethylbutenyl)][BPh$_4$]. A sample of [Fe(P(OMe)$_3$)$_3$(η^3-2,3-dimethylbutenyl)][BPh_4] was treated as in the preceding synthesis. There was no discernible color change in 30 min so an additional portion of *t*-BuNC was added. The mixture was stirred for about 24 h while the color of the solution lightened from orange to yellow. Workup was as described in the preceding synthesis.

Preparation of [Fe(P(OMe)$_3$)$_3$(CO)(η^3-butenyl)][BPh$_4$]. The procedure was analogous to that for the *t*-BuNC reaction except that it was carried out in a serum capped bottle and CO (1.2 mmol) was syringed into the bottle.

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