Metal Atom Synthesis of Iron Diene Phosphite Complexes

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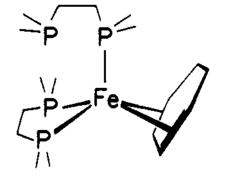
Abstract: Complexes of the type Fe(η^4-diene)L_3 (where L are phosphorus ligands) have been prepared for a variety of simple cyclic and acyclic dienes by metal atom evaporation techniques. In addition, complexes of the type Fe(η^4-diene)$_2$L have been prepared for acyclic dienes. The Fe(diene)L_3 complexes show temperature-dependent ^{31}P{^{1}H} NMR behavior; analysis of these spectra yields mechanistic information concerning the nature of the rearrangement process. Iron atom evaporation syntheses with cyclohexadiene and trimethyl phosphite give the additional complexes Fe(η^4-1,3-C_6H_8)(η^2-1,4-C_6H_8)L_2, Fe(η^6-C_6H_6)L_2, Fe(η^6-C_6H_6)(η^4-1,3-C_6H_8), and FeP_2(η^5-cyclohexadienyl)(hydride). Species related to the latter compound are cited as intermediates in proposed mechanisms for several observed hydrogen-transfer reactions including the conversion of cyclohexadiene to benzene and cyclohexene.

Introduction

A recent review[1] points out the importance of carbonyl compounds in the organometallic chemistry of iron. Of almost 400 references covering organometallic iron complexes for the year 1975, only a handful involved systems containing phosphorus ligands and no carbonyls. Thus the wide variety of steric and electronic modifications possible with phosphorus ligands has been almost completely unexplored. This situation arises mainly from a lack of good synthetic techniques to give the necessary starting materials.

A number of preparative methods for Fe(diene)L_3complexes have been reported. Kruck[2] has prepared a variety of Fe(diene)(PF_3)$_3$ complexes by photolysis of Fe(PF_3)$_5$ in the presence of dienes. The corresponding photolysis of Fe(P(OMe)$_3$)$_5$ in the presence of dienes does not provide a good route to Fe(diene)[P(OMe)$_3$]$_3$ compounds.[3] We have recently reported[4] preparation of the complex Fe(η^4-C_6H_8)[$(CH_3)_2PCH_2CH_2P(CH_3)_2$]$_2$ (**1**) and related species involving cyclic



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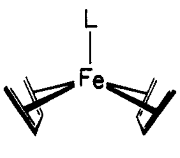
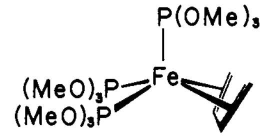
dienes; when acyclic butadiene was employed in the same preparation, both bidentate phosphorus ligands remained chelated with butadiene coordinating in an η^2 manner. Muetterties has reported[5] the preparation of Fe(PMe_3)$_3$(η^4-butadiene) by reduction of $FeCl_2$ in the presence of PMe_3 and butadiene. This technique is general for a variety of diene and triene molecules but does not work with phosphites.[3]

The synthesis of organometallic compounds by the "metal atom evaporation" technique has become well established over the last 5 years.[6] A limited number of communications and notes on the application of this approach to the preparation of organometallic compounds of iron involving phosphorus ligands have appeared.[7-13] Von Gustorf[7] and Skell[8] reported the preparation of the complexes Fe(butadiene)$_2$L, where L



L = CO
PF$_3$
P(OMe)$_3$ (**2**)

= CO and PF_3. Von Gustorf[9] later reported a complex of this type with L = P(OMe)$_3$ as an inseparable mixture with Fe(butadiene)[P(OCH_3)$_3$]$_3$ (**3**). Timms reported the preparation



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of the unstable complex Fe(1,5-COD)$_2$[10] (COD = cyclooctadiene) which serves as a useful precursor to a variety of 1,3- and 1,5-COD complexes.[11,12] A study of intramolecular exchange in a series of Fe(1,3-COD)[P(OR)$_3$]$_3$ complexes has been carried out by analysis of the variable-temperature ^{31}P[^{1}H] spectra.[11,13] We now report the results of a detailed study of the reaction of iron atoms with polyenes in the presence of phosphorus ligands and the nuclear magnetic resonance properties of selected products.

Results

Variations in apparatus design and experimental technique can greatly affect the results of metal atom evaporation syntheses. These effects can range from variation in yields to the generation of completely different products.[14] Therefore, the experimental design must be specified in some detail to allow duplication of the results. The apparatus used in this work is of the vertical fixed flask design.[6] Detailed description of our experimental design and some observations about the metal atom evaporation technique are given in the Experimental Section.

Reactions with Acyclic Dienes. The cocondensation of iron atoms with butadiene on a liquid nitrogen cooled surface followed by reaction of the resultant mixture with P(OMe)$_3$ has been reported[9] to give an inseparable mixture of Fe[P(OMe)$_3$](butadiene)$_2$ (**2**) and Fe(butadiene)[P(OMe)$_3$]$_3$ (**3**). By redesigning the experiments either product can be obtained as desired. Cocondensation of iron atoms with butadiene on a liquid nitrogen cooled surface followed by reaction with a minimum of P(OMe)$_3$ in pentane at about −120°C gives a mixture from which **2** is readily isolated. Iron atoms cocondensed with butadiene and excess P(OMe)$_3$ give a mixture which contains **3** as its major product. Isolation of **3** was accomplished using high-performance, size exclusion, liquid chromatography.[15]

The NMR parameters of **2** and **3** are given in Tables I and II. The ^{31}P[^{1}H] NMR spectrum of **2** is a singlet and invariant with temperature. The trisphosphite complex **3** displays a temperature-dependent ^{31}P[^{1}H] NMR spectrum (Figure 1),

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Table I. $^{31}P\{^1H\}$ NMR Parameters for Metal Atom Evaporation Species

Fluxional Complexes

no.	complex[a]	δ_A[b]	δ_B[b]	J_{AB}[b]	t, °C[d]	ΔH	ΔS	$\Delta G^{\ddagger}_{298}$
3	$Fe(P(OMe)_3)_3$(butadiene)	200.1	177.7	31	−80	10.5	−3.1	11.4
5	$Fe(P(OEt)_3)_3$(butadiene)							
7	Fe(P(O-*i*-Pr)$_3$)$_3$(butadiene)	190.2	177.2	38	−90			
11	$Fe(P(OMe)_3)_3$(isoprene)	A 199.3	B 176.7 C 173.6	AB ±34 AC ±26 BC ±137	−90	10.8	−4.2	12.1
14	$Fe(P(OEt)_3)_3$(isoprene)	A 189	B 173 C 170	AB ±32 AC ±24 BC ±140	−90			
22	$Fe(P(OMe)_3)_3$(DMBD)	196.3	174.0	32	−90	10.0	−7.6	12.3
24	$Fe(P(OEt)_3)_3$(DMBD)	189.6	172.2	31	−90			
27	$Fe(P(OMe)_3)_3H$(ethenylallyl)	186	189	37	0			
28	$Fe(P(OMe)_3)_3H$(isopropenylallyl)	190	185	50	0			
29	Fe(P(O-*i*-Pr)$_3$)$_2$(DMBD)$_2$[c]	192.5	177.6	25	−90			
30	$Fe(P(OMe)_3)_3$COD	180.2	177.9	39	−91	9.9	−2.8	10.7
31	$Fe(P(OMe)_3)_3$CHPD	186.2	177.8	38	−83	9.5	−7.0	11.6
32	$Fe(P(OMe)_3)_3$CHXD	192.5	180.7	39	−126	9.0	+0.7	8.8
33	$Fe(P(OMe)_3)_3$CND	186.4	178.4	37	−80	10.1	−5.0	11.6
34	$Fe(PMe_3)_3$COD	26.6	24.1	5.5	−90	13.60	−3.9	14.8
37	$Fe(P(OEt)_3)_3$COD	181.9	175.5	39	−70	11.7	2.7	10.9
38	Fe(P(O-*i*-Pr)$_3$)$_3$COD	181.6	174.7	36	−70	11.3	−3.3	12.3
39	Fe(P(O-*i*-Pr)$_3$)$_2$(COD)$_2$[c]	189.6	170.0	37	−90			
44	$Fe(P(OMe)_3)_3$COTRI	A 185.6	B 180.3 C 175.9	AB ±42 AC ±32 BC ±105	−90			
47	$Fe(P(OMe)_3)_3$CHT	A 188.6	B 181.7 C 177.7	AB ±49 AC ±35 BC ±103	−90	9.6	−3.4	10.5

Complexes Displaying Single Line Spectra

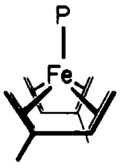
no.	complex	δ_A[b]	no.	complex	δ_A[b]
2	$Fe(P(OMe)_3)$(butadiene)$_2$	201.7	**18**	*cis*-$Fe(P(OPh)_3)$(isoprene)$_2$	176.9
4	$Fe(P(OEt)_3)$(butadiene)$_2$	197.2	**19**	*trans*-$Fe(P(OMe)_3)$(*t*-PD)$_2$	191.4
6	Fe(P(O-*i*-Pr)$_3$)(butadiene)$_2$	188.2	**20**	*cis*-$Fe(P(OMe)_3)$(*t*-PD)$_2$	192.6
8	$Fe(P(OPh)_3)$(butadiene)$_2$	181.2	**21**	$Fe(P(OMe)_3)(DMBD)_2$	202.9
9	*trans*-$Fe(P(OMe)_3)$(isoprene)$_2$	206.0	**23**	$Fe(P(OEt)_3)(DMBD)_2$	188.3
10	*cis*-$Fe(P(OMe)_3)$(isoprene)$_2$	205.3	**25**	Fe(P(O-*i*-Pr)$_3$)(DMBD)$_2$	187.1
12	*trans*-$Fe(P(OEt)_3)$(isoprene)$_2$	191.0	**26**	$Fe(P(OMe)_3)$(*t*,*t*-HD)	187.4
13	*cis*-$Fe(P(OEt)_3)$(isoprene)$_2$	190.4	**41**	$Fe(PPh_3)$(1,5-COD)	−11.8
15	*trans*-Fe(P(O-*i*-Pr)$_3$)(isoprene)$_2$	185.9	**48**	$Fe(P(OMe)_3)_2$(1,3-CHXD)(1,4-CHXD)	183.2
16	*cis*-Fe(P(O-*i*-Pr)$_3$)(isoprene)$_2$	183.3	**50**	$Fe)P(OMe)_3)_2$(BENZ)	178.9
17	*trans*-$Fe(P(OPh)_3)$(isoprene)$_2$	178.1	**51**	$Fe(P(OMe)_3)_2(C_6H_7)H$	185.2

[a] DMBD = 2,3-dimethylbutadiene, COD = cyclooctadiene, CHPD = cycloheptadiene, CHXD = cyclohexadiene, CND = cyclononadiene, COT = cyclooctatetraene, COTRI = cyclooctatriene, CHT = cycloheptatriene, *t*-PD = *trans*-pentadiene, *t,t*-HD = *trans,trans*-2,4-hexadiene, BENZ = benzene, and C_6H_7 = cyclohexadienyl. [b] δ (ppm) downfield from 85% H_3PO_4, J in Hz, AB_2 spin systems except where noted otherwise. [c] AB spin system. [d] Temperature at which slow exchange NMR parameters were determined.

the details of which will be discussed in a later section of this paper. The trimethyl phosphite region of the ^1H NMR spectrum also displays a temperature dependence but, because of complex P–H coupling, resolution is poor even at 220 MHz and detailed analysis would be difficult.

Complexes analogous to **2** and **3** can be prepared using a variety of phosphorus ligands, though in some cases only mixtures of the mono- and bis(diene) products were obtained. The spectroscopic parameters for the analogues of **2** and **3** (complexes **4–8**) are presented in Tables I and II. In the case of nonvolatile ligands such as P(O-*i*-Pr)$_3$ and $P(OPh)_3$ it was not practical to simultaneously cocondense the diene and phosphite with the iron atoms. The phosphite was placed in the reactor as a pentane solution prior to the diene–iron cocondensation. The cocondensation mixture was then washed into the phosphite solution with pentane at −120 °C. For most reactions, we find this technique preferable to the rotary evaporator technique involving a liquid phase, but the rotary flask is invaluable for other reactions not discussed here.

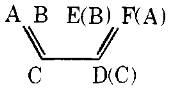
Complexes analogous to **2** and **3** can also be prepared using substituted butadienes. The spectroscopic properties of these complexes (**9–26**) are also listed in Tables I and II. When the unsymmetrically substituted diene, isoprene (2-methyl-1,3-butadiene), is employed, the bis(diene) product is a mixture of two isomers, **9** and **10**. The ratio of trans to cis in the isolated product varies with the steric size of the phosphite. The two products are in a 6:4 (**9:10**) ratio for $P(OMe)_3$ (cone angle[16] θ = 107°), 7:3 (**12:13**) for $P(OEt)_3$ (θ = 109°), 8:2 (**15:16**) for P(O-*i*-Pr)$_3$ (θ = 130°), and 8:2 (**17:18**) for $P(OPh)_3$ (θ = 128°). As the steric requirements of the phosphorus ligand are increased, the dienes are forced closer together and the unfavorable methyl–methyl contact shifts the distribution toward



trans **9**

cis **10**

Table II. ^{1}H and ^{13}C NMR of Metal Evaporation Species

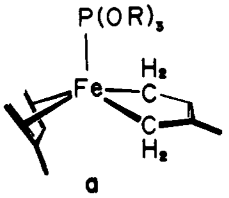


no.	complex^a	NMR data^b
2	Fe(P(OMe)$_3$)(butadiene)$_2$	C, 4.41 (4, t, J = 8); OMe, 3.53 (9, D, J_{PH} = 10); A, 1.00 (4, D, J = 8); B, −0.70 (4, DD, J = 8, 16)
3	Fe(P(OMe)$_3$)$_3$(butadiene)	C, 4.98 (2, t, J = 6); OMe, 3.50 (27, q, J = 3); A, 1.40 (2, M); B, 0.59 (2, t, J = 6)
	Fe(CO)$_3$(butadiene)	C, 4.50 (2, td); A, 1.25 (2, dt); B, 0.23 (2 dd) (AA′BB′CC′)
5	Fe(P(OEt)$_3$)$_3$(butadiene)	C, 3.64 (2, t, 6); OCH$_2$, 4.25 (18, Qm, 7); A, 1.64 (2, M); OCMe, 1.20 (27, T, 7); B, −0.46 (2, Qi, 6).
7	Fe(P(O-*i*-Pr)$_3$)$_3$(butadiene)	OCH, 4.77 (9, M); C, 4.32 (2, M); A, 2.07 (2, M); CMe$_2$, 1.27 (54, D, J = 7); B, −0.73 (2, M)
8	Fe(P(OPh)$_3$)(butadiene)$_2$	*o*-Ph, 7.16 (6, D, 8); *m*-Ph, 7.02 (6, T, 8); *p*-Ph, 6.86 (3, T, 8); C, 4.36 (4, t, 7); A, 1.52 (4, M); B, −0.43 (4, DD, 9, J_{PH} = 17)
15,16	Fe(P(O-i-Pr)$_3$)(isoprene)$_2$	OCH, 4.80 (3, Br); C, 3.9 (2, Br); D-Me, 1.9 (6, Br); OCMe$_2$, 1.25 (18, Br); F, 1.0 (2, Br); A, 0.8 (2, Br); B, −0.8 (2, Br); E, −0.9 (2, Br)
17	*trans*-Fe(P(OPh)$_3$)(isoprene)$_2$	*o*-Ph, 7.41 (6, D, 8); *m*-Ph, 7.06 (6, T, 8); *p*-Ph, 6.87 (3, T, 8); C, 3.79 (2, t, 9); D-Me, 1.70 (6, S); F, 1.31 (2, d); A, 1.12 (2, DD, 8, 2); B, −0.40 (2, DDD, 9, 2, J_{PH} = 18); E, −0.58 (2, DD, 1, J_{PH} = 18)
18	*cis*-Fe(P(OPh)$_3$)(isoprene)$_2$	same as **17** except C, 3.95 (2, t, 9); D-Me, 1.68 (6, s)
19	Fe(P(OMe)$_3$)-*trans*-(*t*-PD)$_2$	C, 4.40 (2, M, J = 5, 7, 9, J_{PH} = 1); D, 4.22 (2 M, J = 8, 5, J_{PH} = 1); OMe, 3.61 (9, D, J_{PH} = 10); A, 0.92 (2, M); Me-F, 0.86 (6, DD, J = 6, J_{PH} = 2); E, −0.23 (DDQ, J = 6, 8, J_{PH} = 14) B, −0.72 (2, DD, J = 9, J_{PH} = 16.5)
21	Fe(P(OMe)$_3$)(DMBD)$_2$	OMe, 3.43 (9, D, J_{PH} = 9); Me-C, 1.73 (12, S); A, 0.91 (4, S); B, 0.74 (4, D, J_{PH} = 20)
23	Fe(P(OEt)$_3$)(DMBD)	OCH$_2$, 4.03 (6, Qi, J = J_{PH} = 7); Me-B, 1.78 (12, S); OCMe, 1.18 (9, T, J = 7); A, 0.95 (4, D, J = 2); B, −0.75 (4, DD, J = 2, J_{PH} = 19.5) ^{13}C{^{1}H}: C, 90.0 (D, J_{PC} = 3); A, 60.2 (D, J_{PC} = 6); OCH$_2$, 38.5 (D, J_{PC} = 18); Me-C, 19.2 (S); OCMe$_2$, 16.4 (D, J_{PC} = 6)
24	Fe(P(OEt)$_3$)$_3$(DMBD)	OCH$_2$, 4.02 (18, M); C-Me, 2.27 (6, S); A, 1.82 (2, d, 2); OCMe, 1.20 (27, T, 7); B, −0.59 (2, m)
25	Fe(P(O-*i*-Pr)$_3$)(DMBD)$_2$	OCH, 4.76 (3, Oc, J = J_{PH} = 6); Me-C, 1.79 (12, S); OCMe$_2$, 1.25 (18, D, J = 6); A, 0.95 (4, D, J = 2); B, −0.80 (4, DD, J = 2, J_{PH} = 20) ^{13}C{^{1}H}: C, 90.2 (D, J_{PC} = 3); A, 68.4 (D, J_{PC} = 9); OCH, 39.3 (D, J_{PC} = 16); OCMe$_2$, 24.6 (D, J_{PC} = 4) Me-C, 19.3 (S)
26	Fe(P(OMe)$_3$)(*t,t*-HD)$_2$	C, 4.42 (4, dd, J = 8, 2); OMe, 3.75 (D, J_{PH} = 10); Me-A, 0.91 (12, DD, J = 6, 2) B, −0.60 (4, DQD, J = 6, 8, J_{PH} = 15) ^{13}C{^{1}H}: C, 79.08 (D, J_{PC} = 3); B, 52.48 (D, J_{PC} = 7); OMe, 50.30 (D, J_{PC} = 12); A, 18.65 (S)
30	Fe(P(OMe)$_3$)$_3$(1,3-COD)	C, 4.89 (2, dt, J = 7, 2); OMe, 3.55 (27, q, J = 3.3); A, 2.87 (2, M); CH$_2$-B, 2.13 (4, M); CH$_2$, 1.56 (4, t, J = 3) ^{13}C{^{1}H}: C, 86.18; OMe, 51.47; A, 50 69; CH$_2$-B, 27.30; CH$_2$, 26.91.
31	Fe(P(OMe)$_3$)$_3$(CHPD)	C, 4.89 (2, M); OMe, 4.02 (27, M); A, 2.52 (2, M); CH$_2$-B, 2.20 (2, M), 2.00 (2, M); CH$_2$, 1.55 (2, M)
32	Fe(P(OMe)$_3$)$_3$(CHXD)	C, 4.89 (2, M); OMe, 3.51 (27, M); A, 2.66 (2, M); CH$_2$-B, 1.90 (2, d, J = 9), 1.58 (2, d, J = 9)
	Fe(CO)$_3$(CHXD)	C, 4.90 (2, M); A, 2.91 (2, M); CH$_2$-B, 1.55 (2, M), 1.35 (2, M)
42	Fe(P(OMe)$_3$)$_3$(COT)	room temp COT, 5.25 (8, S), OMe (27, t, J = 6)
44	Fe(P(OMe)$_3$)$_3$(COTRI)	CH-B, 6.10 (1, td, J = 10,2); CH, 5.96 (1, q, J = 3); C, 5.10 (1, M); D, 5.02 (1, dt, J = 6,2); A, 4.78 (1, t, J = 6), OMe, 3.54 (27, M); F, 3.18 (1, M); CH$_2$, 3.04 (1, M), 1.9 (2, M), 1.65 (1, t, J = 13)
48	Fe(P(OMe)$_3$)$_2$(1,3-CHXD)(1,4-CHXD)	CH(1,4-CHXD), 6.20 (2, q); C, 4.09 (2, M); OMe, 3.33 (18, t); FeCH (1,4-CHXD), 3.24 (2, t); CH$_2$ (1,4-CHXD), 2.8 (4, M); A, 2.50 (2, M); CH$_2$-B, 1.63 (2, M), 1.37 (2, M)
49	Fe(C$_6$H$_6$)(CHXD)	C$_6$H$_6$, 4.82 (6, S); C, 4.50 (2, DD, J = 2, 4); A, 2.45 (2, DTD, J = 4, 2, 1); CH$_2$-B, 1.51 (2, DD, J = 8, 2), 1.20 (2, DD, J = 8, 1)
50	Fe(C$_6$H$_6$)(P(OMe)$_3$)$_2$	C$_6$H$_6$, 4.94 (6, T, J_{PH} = 2.5); OMe, 3.36 (18, T, J_{PC} = 6.0)
51	Fe(P(OMe)$_3$)$_2$(C$_6$H$_7$)H	CH, 6.0 (1, t); CH, 5.5 (2, M); CH, 3.4 (2, M); OMe, 3.33 (18, t); CH$_2$, 2 (2, M); hydride, −18.65 (1, T, J_{PH} = 80)

[a] See Table I for abbreviations. [b] (Relative integration, pattern, coupling constants in Hertz). Abbreviations are S = singlet, D = doublet, T = triplet, Q = quartet, Qi = quintet, Oc = octet, M = multiplet; lower case means approximately. J implies J_{H-H}; other J's are indicated.

the trans isomer. The lower field ^{31}P[^{1}H] NMR peak is attributable to the trans isomer and the higher field peak to the cis isomer in each case.

The product distributions are not at equilibrium, since a mixture of crude **9**, **10**, and Fe[P(OMe)$_3$]$_3$ (isoprene) (**11**) heated at 60°C for 1 h in the presence of a large excess of phosphite shows a decrease in **10** and an increase in **9**. Neither **9** nor **10** reacts with the excess phosphite to give **11**. Some dissociative process must be involved to isomerize **10** to **9**. Since **11** is not formed, complete dissociation of the diene can be ruled out. One possible intramolecular process proposed by Whitlock[17] involves formation of an η^2-diene, rotation about the single bond, and migration of the iron center along the transoid diene. Reversal of the process after migration would give the opposite isomer. Another possible intramolecular process involves the intermediacy of an η^2-di-σ-metallocyclopentene complex.[17] Such an η^2 species would be free to collapse to a normal η^4 species with either side of the diene toward the metal.



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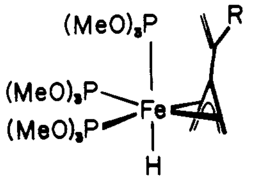
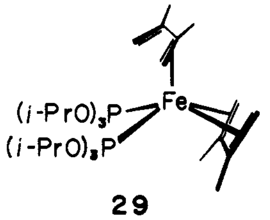
Products which are not of type **2** or type **3** have been observed in the reaction of iron atoms with methylbutadienes. These additional products are observed as minor components of the crude mixtures and can be eliminated by column chromatography; we have been unable to isolate these species to date. The $^{31}P[^1H]$ NMR spectra of these products show tightly coupled AB_2 spin systems. They are stereochemically rigid on the NMR time scale and are very similar to some allyl complexes we have prepared in analogous systems. It is probable that they are formed by hydrogen abstraction from the methyl substituent (configuration **27**). The substituent R would be H for isoprene and Me for 2,3-dimethylbutadiene. Confirmation of this structure will have to await a better method of synthesis or separation.



R = H, **27**
Me, **28**

The cocondensation of iron with 2,3-dimethylbutadiene followed by reaction with $P(O\text{-}i\text{-}Pr)_3$ gives yet another type of product in trace yield. The $^{31}P[^1H]$ NMR spectrum consisted of a singlet at higher temperatures and an AB spin system in the slow exchange limit. The product was not isolated for further characterization; however, we believe that it has structure **29**. Evidence for this structure comes from observation of similar species in the cyclooctadiene-$P(O\text{-}i\text{-}Pr)_3$ system and the isolation and characterization of a related complex in the cyclohexadiene-$P(OMe)_3$ system (vide infra).



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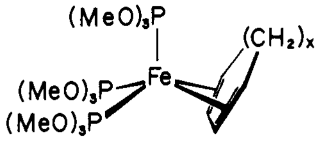
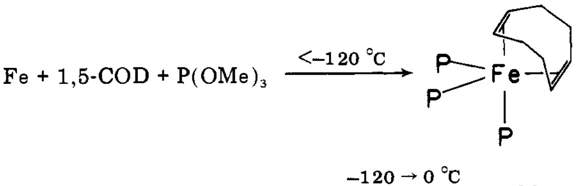
Reactions with Cyclic Dienes. The cocondensation of iron atoms with 1,3-cyclooctadiene and trimethyl phosphite (scheme A) yields the previously reported[11] product, **30**, in yields of up to 30 g. When the reaction is repeated using 1,5-cyclooctadiene (scheme B), one obtains, in the initial stages of workup, a brown oil which deposits an iron mirror when stored for short periods at room temperature. The final product is **30** in low yield. The cocondensation of iron atoms with either 1,3- or 1,5-cyclooctadiene (schemes C and D, respectively) followed by reaction of the resultant mixture with $P(OMe)_3$ at −120 °C gives **30** in moderate to good yields, the reaction with the 1,5 isomer proceeding more cleanly.



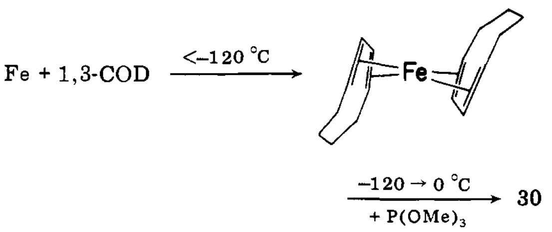
x = 4 **30**
3 **31**
2 **32**
5 **33**

This overall behavior may be explained as follows: scheme A forms **30** directly in highest yield; the intimate mixture of 1,3-COD and $P(OMe)_3$ during the cocondensation gives the product directly or very early during warmup. Scheme B presumably forms the 1,5-diene complex at a temperature too low for isomerization to take place, and once it is formed it decomposes to free iron because of its thermal instability. Schemes C and D give bis(diene) complexes which are stable at reduced temperatures and react with phosphite to give **30** on warming.

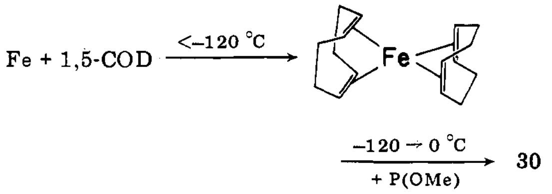
$$\text{Fe} + \text{1,3-COD} + P(OMe)_3 \xrightarrow{<-120\ ^\circ C} \mathbf{30} \qquad (A)$$



(B)



(C)

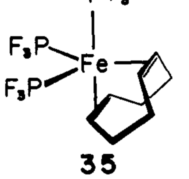


(D)

As with the acyclic diene complexes, the complexes **30, 31, 32,** and **33** are fluxional on the NMR time scale. An analysis of the line-shape behavior of **30** as a function of temperature has been reported elsewhere.[11] The $^{31}P[^1H]$ NMR parameters and the activation parameters are given in Table I and are discussed in a later section.

The trimethylphosphine analogue of **30, 34,** was also prepared. The complex is much less stable than **30** and slowly decomposes at room temperature. The $^{31}P[^1H]$ NMR behavior is similar to that of **30** but with a higher barrier to intramolecular exchange.

Timms has reported that the reaction of PF_3 with Fe(1,5-$COD)_2$ gives **35**, a product in which the 1,5 isomer of COD is



35

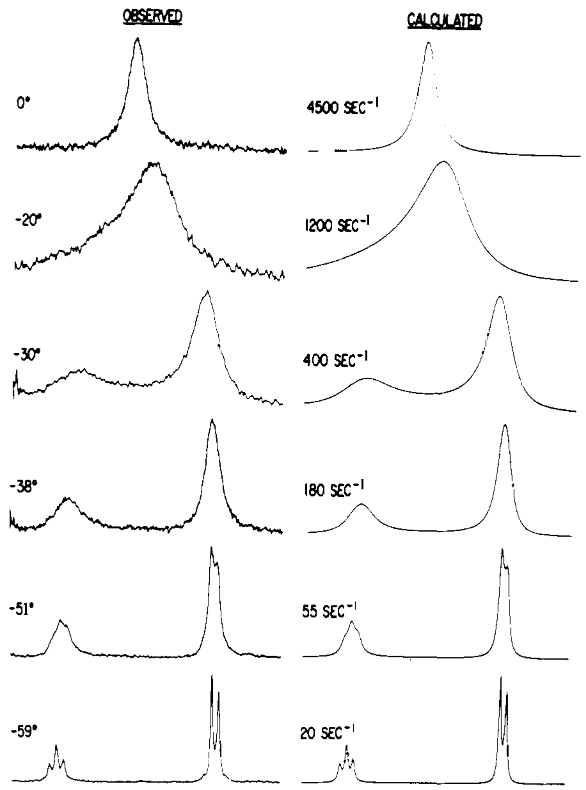
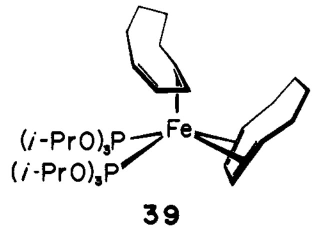


Figure 1. Calculated and observed ^{31}P{^{1}H} NMR spectra of Fe(P(OMe)$_3$)$_3$(butadiene) as a function of temperature.

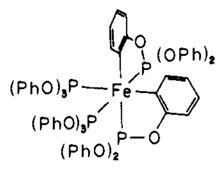
retained.[12] We observe similar behavior. However, the 1,3 isomer **36** is readily prepared by using 1,3-COD in the initial cocondensation with iron atoms and PF$_3$. For the PF$_3$ complexes, the preparation of choice remains that of Kruck[2] involving photolysis of Fe(PF$_3$)$_5$ in the presence of the appropriate diene. Metal atom synthesis of Fe(PF$_3$)$_5$ can be carried out in very high yield.[6] The attempted preparation of **30** from Fe(P(OMe)$_3$)$_5$ gave unsatisfactory results.[3]

The P(OEt)$_3$ analogue of **30**, **37**, whose synthesis has been reported previously,[11] was prepared by method A. The low volatility of triisopropyl phosphite precluded its condensation into the reaction vessel. Therefore, a solution in pentane was frozen at the bottom of the reaction vessel. Iron was cocondensed with 1,5-COD to form Fe(1,5-COD)$_2$ and the mixture was washed to the bottom of the reaction vessel with pentane at −110 °C (scheme D). Though only one product, Fe[P(O-*i*-Pr)$_3$]$_3$(η^4-1,3-COD) (**38**), was isolated from the resultant mixture, a second product, **39**, was detected spectroscopically as a minor component of the crude mixture. The ^{31}P[^{1}H] NMR spectrum (Table I) of this product displayed a single line at room temperature and an AB spin system in slow exchange at −80 °C.



39

As previously reported,[18] the reaction of Fe(1,5-COD)$_2$ with P(OPh)$_3$ gives the unusual doubly ortho-metalated species, **40.** When the same reaction was carried out with triphenylphosphine, a very unstable mixture resulted. The brown material obtained gave iron mirrors even at −20 °C. The ^{31}P[^{1}H] NMR spectrum displayed two singlets, one for free PPh$_3$ with the other to slightly higher field. On filtering to remove precipitated iron metal and rerecording the spectrum, the relative intensity of the free PPh$_3$ singlet had increased. Well-resolved ^{1}H NMR spectra were not obtained because of the continuous formation of iron metal. The upfield chemical shift of the second phosphorus resonance is consistent with an arene-diene complex such as **41.** Similar thermal instability has been observed[3,13b] for other arene-diene complexes involving 1,5-cyclooctadiene.



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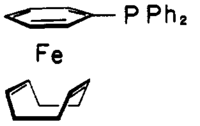
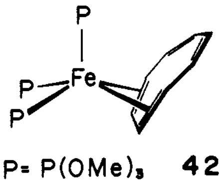


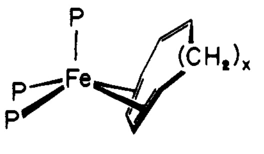
41

The cocondensation of iron atoms with phosphites and cyclooctatetraene yields the dark red, crystalline products **42** and **43.** These complexes are more conveniently prepared by the reaction of excess phosphite with Fe(COT)$_2$.[19] Both the ^{31}P[^{1}H] and ^{1}H NMR spectra of these complexes display line-shape effects as a function of temperature. The fluxional processes, which involve both phosphite and ring exchange, will be discussed elsewhere.[19]



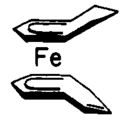
P= P(OMe)$_3$ **42**
P(OEt)$_3$ **43**

The cocondensation of iron atoms with P(OMe)$_3$ and 1,3,5-cyclooctatriene gives **44** as the major product, but trace quantities of **30** and **42** are also observed. Analysis of the composition of the starting triene showed no detectable cyclooctadiene or cyclooctatetraene. Analysis of the volatile materials from the metal atom reactor after the cocondensation showed appreciable quantities of cyclooctadiene and cyclooctatetraene in the residual cyclooctatriene-P(OMe)$_3$-pentane mixture. Stirring a sample of **44** in pure cyclooctatriene did not cause disproportionation to COD and COT, so the transformation presumably took place before all three phosphite molecules were coordinated.



x = 2. **44**
1. **47**

In another experiment, iron atoms were cocondensed with 1,3,5-cyclooctatriene, and the resultant mixture was reacted with P(OMe)$_3$. The only product isolated was a dark red, thermally unstable material containing no phosphite ligands. This material was **45** based on its mass spectrum, complex ^{1}H NMR, and analogy to the previously reported[20] complex **46.** Complex **46** is obtained by the cocondensation of iron atoms



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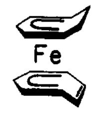
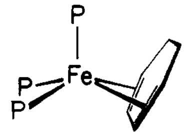


46

with 1,3,5-cycloheptatriene. The transfer of a single hydrogen atom from one coordinated triene to another in these complexes suggests a possible stepwise mechanism for disproportionation of triene to tetraene and diene.

When iron atoms are cocondensed with 1,3,5-cycloheptatriene and the resultant mixture is reacted with $P(OMe)_3$, the yield of the desired product **47** is very low compared to the yield of **46.** If the iron atoms are cocondensed simultaneously with the triene and excess $P(OMe)_3$, **47** is obtained in good yield along with some **46** which is removed by recrystallation. In contrast to the η^4-tetraene complex **42,** neither of the η^4-triene complexes (**44** or **47**) displays exchange of the coordinated and uncoordinated olefinic groups on the NMR time scale at temperatures up to the point at which decomposition becomes rapid. This behavior is consistent with that of the carbonyl analogues.[21]

The cycloheptadiene and cyclononadiene analogues of **30** (**31** and **33**) are isolated as the only products from their respective iron atom reactions. In contrast, a variety of products are isolated from the corresponding cyclohexadiene reactions. When either 1,3- or 1,4-cyclohexadiene is cocondensed with iron atoms and the resultant mixture reacted with $P(OMe)_3$, four organometallic products (**32, 48, 49,** and **50**) are obtained.



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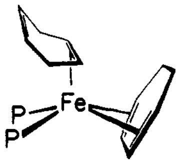

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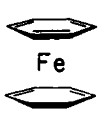

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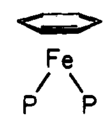
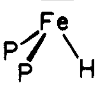


50

There seems to be no difference in the product distribution using the 1,3 or 1,4 isomers of cyclohexadiene. The volatile portion of the reaction mixture is found to contain cyclohexene, cyclohexadienes, and benzene (in addition to the added pentane and $P(OMe)_3$). This catalytic disproportionation of the cyclohexadienes to cyclohexene and benzene has been reported before.[8] After the more volatile components have been distilled from the reaction mixture, the benzene–cyclohexadiene product, **49,** is readily isolated by sublimation. The product obtained in highest yield, **48,** is unusual in that it contains both η^4-1,3- and η^2-1,4-cyclohexadienes. The desired product **32** is obtained in low yield as a mixture with **50.** Separation of these two products by column chromatography results in considerable loss in yield.

When the above reaction is carried out as a simultaneous cocondensation of iron atoms with 1,3-cyclohexadiene and $P(OMe)_3$, the major product, obtained in higher overall yield than all of the products combined from the previous reaction, is the yellow, crystalline material, **32.** The other product, detected as a minor component in the crude **32,** is **51.** Observation of this cyclohexadienyl hydride is significant in that it serves as a model for an intermediate in the hydrogen-transfer process which has been cited in preceding reactions. A mechanism such as scheme E could produce benzene and cyclohexene from cyclohexadiene through hydrido intermediates such as c and e. Intermediate d involves a coordinated aliphatic hydrogen atom similar to those observed in other coordinatively unsaturated iron(II) species.[22]



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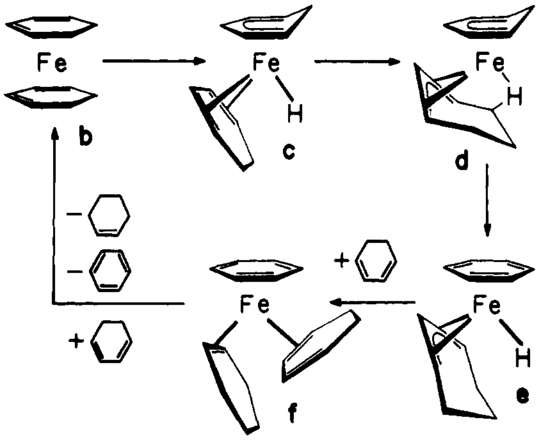
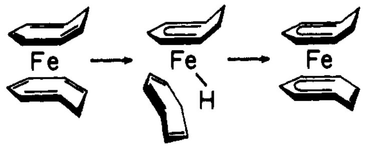


(E)

A species related to **51** or more particularly c would also be a likely intermediate in the formation of the dienyl–trienyl complexes **45** and **46** from bis(triene) precursors. This mechanism would predict hydrogen transfer to an η^4-triene to occur endo with respect to the metal. If the reaction is intermolecular, exo hydrogen atom transfer might be expected based on recent work by Brookhart.[23]



Exchange Mechanism in Fe(diene)L_3 Species. It is generally accepted that Fe(diene)L_3 compounds have the "square pyramidal" geometry used in figures throughout this paper. Evidence comes largely from X-ray studies in the solid state,[24-26] which have to be treated with some caution when considering solution data. For the purposes of the present discussion, a square pyramidal geometry such as that shown for **3** will be assumed. The $^{31}P[^1H]$ spectrum for each of the complexes is temperature dependent, consistent with fluxional character.

Fluxional behavior in iron-diene complexes was first reported for Fe(butadiene)(CO)$(PF_3)_2$.[27] Numerous descriptions of nonrigidity in M(diene)L_3 systems have appeared[11,27-39] and the fluxional behavior has been considered from a theoretical point of view.[40]

In the original work of Warren and Clark,[27] three physical mechanisms were considered for exchange in Fe(butadiene)$(PF_3)_2$(CO) (the complex was shown to be square pyramidal in solution with a phosphine in the apical position). The mechanisms were pairwise exchange of the axial with a basal phosphorus, a concerted twist of the three phosphorus ligands, and rotation of the butadiene. No mechanistic distinction could be made, although the first mechanism seemed unlikely. Mechanistic arguments in favor of the second or third types of exchange have been proposed[32] based on ^{19}F NMR studies of Fe(isoprene)CO$(PF_3)_2$. The observation that the two phosphorus ligands (one of which is apical in the equilibrium geometry) do not become equivalent in fast exchange is evidence for a concerted three-ligand mechanism or for olefin rotation.

NMR studies of the system Ru(butadiene)$[P(C_6H_5)_3]_3$

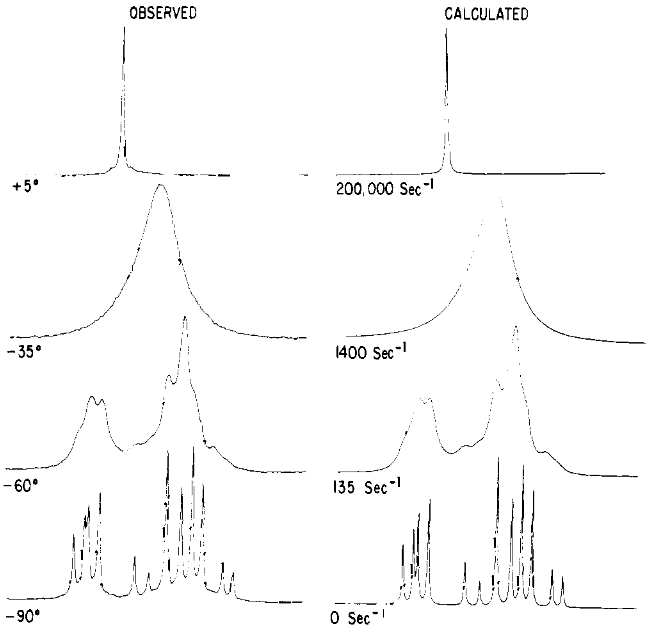
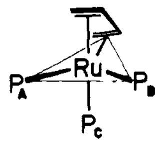


Figure 2. Calculated and observed $^{31}P\{^1H\}$ NMR spectra of Fe(P-(OMe)$_3$)$_3$(cycloheptatriene) as a function of temperature.

suggest behavior quite different from that of the other systems considered in this paper.[38] At room temperature the $^{31}P[^1H]$ NMR shows an AB_2 spin system while at low temperatures it is ABC. Thus, the complex appears to be "trigonal bipyramidal", as in configuration g. Up to room temperature only



g

phosphorus ligands A and B are rendered equivalent (if indeed the exchange is (AB), it cannot proceed by a Berry process,[44] since that would necessarily involve P_c).

Except for this one very unusual case, prior to our recent communication,[13] no direct mechanistic information had been obtained from diene complexes with ML_3 fragments in which the three ligands are identical. Mechanistic studies for this case have the advantage that there is only one isomer present in the system so that varying populations and the presence or absence of a given isomer are not complicating factors.

The observed symmetrical collapse of the three carbonyl resonances for asymmetric diene and heterodiene complexes of $Fe(CO)_3$ is a necessary but not sufficient condition for cyclical exchange.[37] For instance, a two-site exchange problem at coalescence has $k_{12} = (\delta_{12}^2 + J_{12}^2)^{1/2}$. In a three-site problem exchanging by the mechanism (I + II) (vide infra), symmetrical collapse requires that coalescence of the peaks for ligands 1 and 2 occurs at the same temperature as coalescence of the peaks for ligands 1 and 3. The necessary and sufficient condition for this to obtain is that at some temperature T

$$\begin{aligned} k_{12} &\approx (\delta_{12}^2 + J_{12}^2)^{1/2} \\ \text{and } k_{13} &\approx (\delta_{13}^2 + J_{13}^2)^{1/2} \end{aligned} \quad (1)$$

In other words, the approximate conditions (eq 1) will lead to symmetrical collapse, while allowing independent temperature variations of rate constants k_{12} and k_{13}. Simulations were carried out to demonstrate this point conclusively.

The $^{31}P[^1H]$ NMR and activation parameters for Fe(diene)L_3 complexes are presented in Table I. The narrow range of energies of activation for these species suggests that the nature of the exchange process is the same in all cases. As noted previously,[37] steric constraints in these species are relatively minor; changes in ligand cone angle[16] and substituents on the diene cause little change in the activation parameters. This is in contrast to FeL_5 complexes, in which steric effects were found to be important.[42] The $^{31}P[^1H]$ slow exchange spectra for complexes having symmetrical dienes are AB_2 spin patterns as shown for the representative case of **3** in Figure 1. No mechanistic information can be derived from the temperature-dependent behavior of these spectra. Complexes of unsymmetrical olefins give a slow exchange ABC spin pattern (as shown in Figure 2 for **53**) allowing the possibility of mechanistic distinctions.

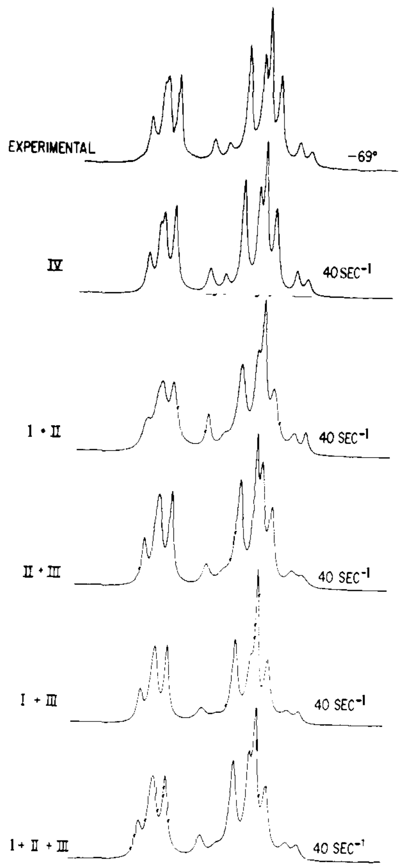


Figure 3. $^{31}P\{^1H\}$ NMR spectra of Fe(P(OMe)$_3$)$_3$(cycloheptatriene) calculated using mechanisms IV, I + II, I + III, II + III, and I + II + III compared with experimental.

For the systems with ABC limiting slow exchange $^{31}P[^1H]$ NMR spectra, all possible permutations and linear combinations of permutations of the group S_3 are allowed exchange processes. The basic permutations of the group S_3 are

E = (A)(B)(C)	I(AB)	IV(ABC)
	II(AC)	(ACB)
	III(BC)	

Because the $^{31}P[^1H]$ spectra collapse to single lines in the fast exchange limit, only basic permutation IV and linear combinations of permutations need be considered in the mechanistic analysis.

We have already demonstrated[13] that for the isoprene complex, **11**, exchange takes place by the permutations IV. The cycloheptatriene complex **47** displays similar behavior. Figure 3 shows a comparison of the experimental spectra of **47** at the rate (temperature) most sensitive to the permutational mechanism with calculated spectra for the five possible mechanisms: IV, I + II, I + III, II + III, and I + II + III. As found for the isoprene complex, only case IV agrees with experiment; the physical mechanism producing the line-shape behavior must result in cyclical exchange of the three phosphorus nuclei. It seems reasonable that this is the exchange mechanism for all Fe(diene)L_3 complexes whether the diene is cyclic or acyclic.

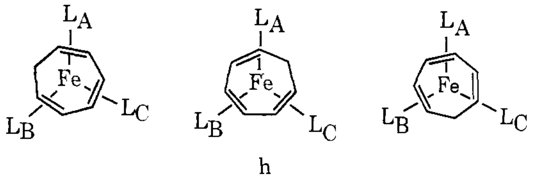
The rate constants for the permutations within a linear combination were assumed to be equal in simulating the effects of the linear combinations of permutations. Since this is not required by symmetry, one could conceive of adjusting the rate constants relative to one another to achieve better agreement with experiment for a given combination. Simulations were carried out with relative rate constants adjusted to achieve better agreement with experiment for a given combination, but in no case could a fit as good as that for IV be obtained. Additionally, arbitrary rate constants are rendered unlikely by observation of the same type of line-shape behavior in all systems studied. Of course, any linear combination which is mainly set IV with small admixtures of the other sets could not be distinguished from IV alone.

Only two categories of physical motion can give rise to type IV behavior; these are "rotation" of the diene or cyclical exchange of the three phosphorus ligands. Differentiation of these two categories is partially semantic, depending on the definition of a coordinate system for viewing the molecule. The more important process can, in principle, be determined by assigning changes in barrier, from one compound to another, to factors which influence primarily the diene bonding and steric situation or the phosphorus ligand bonding and steric situation.

The $\Delta G^{\ddagger}$ values for constant diene (cyclooctadiene) are 10.7, 10.9, 12.3, and 14.8 kcal mol^{-1} for L = P(OMe)$_3$, P(OEt)$_3$, P(O-*i*-Pr)$_3$, and P(Me)$_3$, respectively. For comparison of steric effects, the ligand cone angles[16] are 107, 109, 130, and 118°, respectively. The Tolman ligand electronic effects[16] are 2079.5, 2076.3, 2075.9, and 2064.1 cm^{-1}, respectively. The results suggest a predominantly electronic effect on the barrier height. Relative to the phosphite ligands, the introduction of P(Me)$_3$ increases the net electron density on the metal center. Significant variations in diene steric effects also caused minimal variation activation parameters. The largest change caused by diene variation was observed for cyclohexadiene and was presumably electronic in nature; cyclohexadiene is the only diene which had any appreciable ring strain.

The cyclical exchange mechanism for Fe(diene)L_3 compounds has variously been described as a Bailar twist,[43] a Berry pseudorotation,[41] and a turnstile process.[44] The Bailar twist was formulated for octahedral coordination and would be appropriate if the electronic description of the complexes contained a significant contribution from a (π, 2σ) valence bonding formulation for the diene. The complexes appear to be adequately described by conventional five-coordinate bonding concepts. The Berry-type process involves interconversion of various square pyramidal structures through trigonal bipyramidal intermediates. Two sequential Berry rearrangements are required to correspond to the observed permutational behavior, but such a mechanism cannot be ruled out.

A mechanism of the turnstile type or a rotation of the olefin is the most reasonable cyclical physical process to associate with the permutational behavior defined by IV. Both the turnstile mechanism and diene "rotation" can be pictured schematically as in configuration h. Even if a distinction between these two processes is meaningful, they cannot be distinguished in the present case.



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Conclusions

Metal atom evaporation can provide a synthetically useful route to a variety of iron complexes involving phosphorus ligands and dienes. The possibility of undesired byproducts must be considered, but by careful experimental design this problem can be minimized. After the cocondensation has taken place, but before the iron atoms have attained 18-electron systems, C–H bond cleavage and hydrogen migration reactions are not uncommon. Once 18-electron systems have been obtained, the complexes are kinetically inert to further reactions. This intermolecular kinetic stability does not preclude rapid intramolecular rearrangement in the zerovalent, five-coordinate species. Electronic effects play an important role in the determination of activation parameters for the intramolecular exchange.

Addition of substituents to the diene appears to have little effect on the activation barrier for mutual exchange, indicating that steric effects are of minimal consequence. Incorporation of the 1,3-diene moiety in a carbocyclic structure induces significant shielding of the axial phosphite and slight deshielding of the equatorial phosphites for reasons that are unclear at present. The enthalpy of activation for phosphorus exchange is apparently dependent on ring size of the diene. Cyclononadiene is essentially an acyclic diene but decreasing ring size tends to decrease the activation parameters. At present we have no good rationale for this observation.

For complexes having mirror symmetry, the possible phosphorus exchange permutations of the three phosphorus nuclei are indistinguishable. When asymmetry is introduced to the system by unsymmetrical substitution of the diene, detailed analysis of the temperature-dependent $^{31}P[^1H]$ NMR spectra allows a number of mechanisms to be distinguished; simultaneous permutation of all three nuclei is the observed mechanism. This is interpreted as a rotation of the olefin with respect to the FeL_3 system.

Experimental Section

The metal atom evaporation syntheses were carried out in a modified version of the apparatus developed by Skell[45] and more recently described in "Cryochemistry".[6] The pumping system consisted of a 3-in. oil diffusion pump backed by a high-capacity, two-stage mechanical vacuum pump, with a liquid nitrogen cooled trap between the reaction chamber and the pumping system. The heater for vaporization of the metal consisted of a 5-mL alumina crucible with an integral tungsten filament (G.T.E. Sylvania Emissive Products) suspended by two water-cooled electrodes. The two electrodes were insulated from the metal head of the evaporator by Nylon male connectors (CAJON Ultra Torr) protected from radiant heat and metal vapors by thin metal disks immediately below them. The crucible was powered by a 220-V Variac run through a step-down transformer capable of delivering greater than 70 A at 25 V. Typically, the crucible is charged with about 15 g of lump metal (no powders). The heavy-wall (0.5 cm) glass flask which is immersed in liquid nitrogen during the synthesis is 20 cm in diameter by 36 cm deep. It is connected to the solid brass head of the apparatus by a 6-in. glass flange and "O" ring seal of Viton fluorocarbon rubber and secured by a McCarter clamp (Lab Glass, Inc.). Volatile ligands to be cocondensed with the metal atoms are stored in calibrated 200-mL cylinders sealed with screw-type high-vacuum stopcocks of Teflon fluorocarbon resin (Kontes Glass Co.). The vaporized ligands are carried to the apparatus through heated glass tubing and introduced into the reaction flask through a glass shower head connected to the top of the brass head by a brass ball joint. The ligand introduction system is also connected to a mechanical vacuum pump and a source of argon for flushing the entire apparatus with an inert atmosphere.

The iron atoms are typically evaporated at a rate of 3-5 g/h for 2-4 h. The ligands are condensed into the reactor from graduated cylinders at rates of 0.5-2.0 mL/min. Iron evaporation rates of 0.5-10 g/h and ligand rates of 0.1-4 mL/min have been employed. Highest percent

Table III. Analytical Results for Metal Atom Evaporation Species

no.	complex[a]	mp,[b] °C	anal.[c] C	H	P	mass spectrum[c] parent	loss	ion	loss	ion
2	Fe(P(OMe)$_3$)(butadiene)$_2$	78	45.9	7.4	10.8	288.0576	−BD	234.0107		
			45.6	6.5	11.0	288.0581		234.0115		
3	Fe(P(OMe)$_3$)$_3$(butadiene)	218	32.4	6.9	19.2					
			32.1	6.7	20.4					
7	Fe(P(O-*i*-Pr)$_3$)$_3$(butadiene)	156	50.7	9.5	12.7	734	−BD	680		
			51.1	9.3	12.7	734		680		
11	Fe(P(OMe)$_3$)$_3$(isoprene)	219	33.9	7.1	18.7	496.0890	−OMe	465.9676		
			33.5	6.8	19.4	496.0865		465.9666		
15, 16	Fe(P(O-*i*-Pr)$_3$)(isoprene)$_2$					400.1828	−isop	332.1202		
						400.1865		332.1224		
17, 18	Fe(P(OPh)$_3$)(isoprene)$_2$					502.1358	−isop	434.0733	−2isop	366.0107
						502.1423		434.0754		366.0106
19	Fe(P(OMe)$_3$)(*t*-PD)$_2$	70	49.4	8.0	9.8	316.0889	−*t*-PD	248.0263	−2*t*-PD	179.9639
			49.7	7.7	10.0	316.0877		248.9778		179.9608
21	Fe(P(OMe)$_3$)(DMBD)$_2$	75	52.3	8.5	9.0	344.1202	−DMBD	362.0420	−P(OMe)$_3$	220.0914
			52.3	8.2	9.4	344.1231		362.0426		220.0935
22	Fe(P(OMe)$_3$)$_3$(DMBD)	191	35.3	7.3	18.2					
			35.1	7.4	18.9					
24	Fe(P(OEt)$_3$)(DMBD)	82	45.3	8.7	14.6					
			45.3	8.9	14.9					
25	Fe(P(O-*i*-Pr)$_3$)(DMBD)$_2$	52	52.0	9.6	12.2					
			52.3	9.4	14.0					
26	Fe(P(OMe)$_3$)(*t,t*-HD)$_2$	64	52.3	8.5	9.0	344.1202				
30	Fe(P(OMe)$_3$)$_3$(COD)		52.5	8.7	8.9	344.1231				
37	Fe(P(OMe)$_3$)$_3$(CHPD)	216	36.8	7.1	17.8	522.0987	−CHPD	428.0216	−P(OMe)$_3$	398.0709
			36.7	7.0	17.6	522.0997		428.0232		398.0733
32	Fe(P(OMe)$_3$)$_3$(CHXD)	212	35.5	6.9	18.3	508.0841	−CHXD	428.0216	−P(OMe)$_3$	384.0552
			35.7	6.9	18.3	508.0844		428 0192		384.0581
42	Fe(P(OMe)$_3$)$_3$COT	122	38.4	6.6	17.5	532.0841	−COT	428.0216	−P(OMe)$_3$	408.0553
			38.6	6.6	17.2	532.0889		428.0192		408.0590
44	Fe(P(OMe)$_3$)$_3$COTRI	174	38.2	7.0	17.4	534.0997	−COTRI	428.0216	−P(OMe)$_3$	410.0709
			38.5	6.9	17.4	534.1018		428.0200		410.0686
48	Fe(P(OMe)$_3$)$_2$(1,4-CHXD)(1,3-CHXD)		46.6	7.3	13.4	464.1178	−2CHXD	303.9927		
			47.0	7.1	14.1	464.1187		303.9945		
49	Fe(C_6H_6)(1,3-CHXD)	109	67.3	6.6		214.0463	−CHXD	133.9833		
			67.4	6.6		214.0444		133.9819		
50	Fe(P(OMe)$_3$)$_2$(BENZ)	39	37.7	6.3	16.2					
			37.3	6.5	17.1					

[a] See Table I for abbreviations. [b] Under nitrogen, uncorrected. [c] Calculated above found.

yields based on metal evaporated are obtained at low rates of metal atom deposition and high dilution in ligand; however, the highest yields of isolated material per hour were obtained under the typical conditions noted. Other variables to be considered are the quantity of coolant consumed (most reactions described here consume ~200 L of liquid nitrogen) and the cost of the ligands chosen. It takes about 10% more power to increase the metal atom evaporation rate from 0.5 to 4 g/h; most of the power applied to the system is lost as radiant energy, not as the heat of vaporization of the metal. This radiant energy must be carried away through the walls of the reaction flask, and constitutes a coolant loss. It is therefore advantageous to insulate the crucible with metal oxide fiber and, in some cases, to surround it with a water-cooled heat shield; either of these measures can cut liquid nitrogen consumption dramatically.

Optimization of reaction conditions to obtain the best net yield was carried out using the system cyclooctadiene-trimethyl phosphite-iron. The established conditions were then used for subsequent reactions with other ligands, with only slight variations.

All manipulations after the cocondensation reactions were carried out in the dry nitrogen atmosphere of a Vacuum Atmospheres drybox or on a standard vacuum line. Melting points were measured under nitrogen and uncorrected. The $^{31}P[^1H]$ NMR spectra were recorded on a Bruker HFX-90 spectrometer at 36.43 MHz. Proton spectra were recorded using Varian HR-220 and XL-100 spectrometers, the latter for [^{31}F] and [^{1}H] decoupling and variable-temperature experiments. ^{13}C NMR spectra were recorded on a Bruker WH-90 spectrometer. High-resolution mass spectra were recorded on a CEC 21-110B spectrometer. Analyses were carried out at our analytical facilities (see Table III for results).

1,3,5-Cyclooctatriene was prepared by hydrolysis of the cyclooctatetraene dianion.[46] 1,3-Cyclononadiene was prepared from cyclooctene by addition of dibromocarbene to give dibromobicyclononane, methyllithium reduction to give 1,2-cyclononadiene, and isomerization with KO-*t*-Bu in dimethylformamide.[47] The other diolefins were commercially available and were used after filtration through neutral-grade alumina and degassing. The phosphorus ligands were commercially available and were used after purification and degassing. Solvents were dried by standard techniques.

Cocondensation of Butadiene and Iron in the Presence of P(OMe)$_3$. Iron (12.2 g, 0.2 mmol) was cocondensed with butadiene (130 mL, 2.0 mol) onto a liquid nitrogen cooled surface over 2 h. Then a layer of P(OMe)$_3$ (25 mL, 0.2 mmol) was added followed by a final layer of ether (60 mL). The mixture was allowed to warm to room temperature with stirring. After 30 min, the excess butadiene was distilled from the reactor and the sample was transferred to a drybox. The suspension was filtered through Celite and stripped to an oil under vacuum. The oil was taken up in pentane, filtered through Celite, and chromatographed on alumina to yield a yellow solution. Stripping on a vacuum line resulted in a yellow oil. $^{31}P[^1H]$ NMR indicated a mixture of two species in approximately equal concentration, both having singlets at room temperature (201.7 and 185.7 ppm). When the temperature was lowered to −80 °C, the higher field resonance split into an AB_2 spin system (see Table I for $^{31}P[^1H]$ NMR parameters). The mass spectrum indicated a mixture of Fe(C_4H_6)$_2$P(OMe)$_3$ and Fe(C_4H_6)(P(OMe)$_3$)$_3$. Thus the low-field resonance is attributable to the monophosphite complex **2**, and the higher field resonance is attributable to **3**. Attempted separation of these two complexes by sublimation, crystallization, and conventional chromatography was unsuccessful.

Preparation of Fe(butadiene)$_2$(P(OMe)$_3$). The preceding procedure was employed, but the $P(OMe)_3$ was placed in the reactor as a pentane solution prior to evaporation of metal. The butadiene-iron condensate then had to melt and flow down to the phosphite before reaction could take place. This gave a mixture of products which was very rich in the bis(diene) species. After removal of phosphite, the bis(diene) species was crystallized from pentane at −50 °C to give an orange-yellow product (yield 10 g). There was a lesser amount (about 5 g) of the bis(diene) product left in the pentane filtrate, but it could not be collected without contamination by some of the residual monodiene species.

Preparation of Fe(butadiene)(P(OMe$_3$)$_3$. Iron (15 g) was cocondensed with butadiene (70 mL) and $P(OMe)_3$ (140 mL) on a liquid nitrogen cooled layer of pentane over 3.5 h. A second layer of pentane was condensed, and the mixture was allowed to warm to room temperature over 3 h. This procedure gave a mixture of products rich in the desired monodiene species. Workup involved Celite filtration, removal of volatiles under vacuum, and chromatography on alumina. A small amount of material could be obtained free of the bis(diene) species but most of the material coming off the column was contaminated with the bis(diene) species (yield 18 g, crude). The two species are readily separated by size-exclusion liquid chromatography. The technique used has been described elsewhere.[15] The column consisted of four 0.3-m (7.8-mm diameter) columns (Waters Microstyrogel 100 Å) used in series. The elution corresponds to molecular size with **3** eluting before **2** (29.3 mL for **3** and 33.0 mL for **2**) in THF at a flow rate of 1.5 mL/min.

Other diene species were prepared and isolated similarly. Physical properties are given in Tables I and II.

Cis to Trans Isomerization. A portion of the final crude mixture from the cocondensation of iron, isoprene, and trimethyl phosphite was mixed in toluene with a 20-fold excess of $P(OMe)_3$. The $^{31}P[^1H]$ NMR spectrum showed **9**, **10**, and **11** in the ratio of 42:30:38 (normalized by the sum of their total intensities = 100). After heating at 62 °C for 24 h, the ratio was 54:8:38. **10** was converted to **9** but there was no change in the relative concentration of **11**.

Reaction of PPh$_3$ with Fe(COD)$_2$. Iron (9.9 g) was condensed into 1,5-cyclooctadiene (120 mL) on a liquid nitrogen cooled surface over 2.5 h. This was mixed with pentane and allowed to stir with PPh_3 at −100 °C for 20 min before warming to room temperature. The suspension was filtered and then stripped to an oil. Toluene extraction followed by filtration led to a dark red-brown solution which precipitated a small residue when ether was added. The solution was stripped to an oil which was extracted with ether. The residue gave no ^{31}P signal. The ether solution gave several resonances at the chemical shift of free PPh_3 and above. A crystalline product was not isolated and the solution was constantly depositing iron metal as the product decomposed. Further characterization was not attempted.

Preparation of Fe(1,3-COD)(PMe$_3$)$_3$. Iron (4.95 g) was cocondensed with 1,5-cyclooctadiene (170 mL) over 3 h onto a −196 °C surface. A layer of PMe_3 was condensed in on top of this and finally a layer of pentane was condensed in. The mixture was allowed to melt and stir at −78 °C. It was then quickly filtered through Celite and stripped to tacky black solids. Treatment with Darco followed by Celite filtration yielded a green solution which gave green solids upon stripping. Chromatography of a pentane solution on alumina did little good. Crystallization at −50 °C gave yellow crystals. The compound is unstable at room temperature. NMR spectra were obtained on freshly Millipore filtered solutions at reduced temperatures. The variable temperature ^{31}P spectrum is shown in Figure 3.

Preparation of Fe(C$_7$H$_7$)(C$_7$H$_9$). Iron (11.6 g, 0.2 mol) was cocondensed with cycloheptatriene (100 mL, 1 mol) onto a liquid nitrogen cooled surface over 3 h. This was followed by a layer of pentane (60 mL). This mixture was allowed to melt and was stirred with $P(OMe)_3$ (25 g, 0.2 mol) at −120 °C. This was allowed to warm to −78 °C and stirring was continued for 1 h. The dark red-brown suspension was filtered through Celite and the residue was washed with pentane. The combined filtrate was stripped to dryness on a vacuum line. The solids were extracted with pentane and chromatographed on alumina to yield a red solution. The solution was treated with Darco and then filtered through Celite; reduction in volume and cooling for 24 h at −40 °C gave a dark red, crystalline product, yield 12 g.

At 80 °C, the ^1H NMR of the η_5-C_7H_7 is a single line because of rotation of the ring. The η_5-C_7H_9 shows five different resonances in the ratio of 1:2:2:2:2; the geminal methylene hydrogen atoms are nonequivalent because two are up and the other two are down. At room temperature, the exchange of the η_5-$C_7H_7^-$ has been slowed so that there are four resonances in the ratio of 1:2:2:2. The η_5-$C_7H_9^-$ is relatively unchanged. At −80 °C the η_5-C_7H_9 has developed a pucker, making the two methylene carbon atoms nonequivalent. This results in inequivalencies around both rings and a very complex spectrum.

Preparation of Fe(η_4-cycloheptatriene)(P(OMe)$_3$)$_3$. Cycloheptatriene (140 mL, 125 g, 1.35 mol) and $P(OMe)_3$ (150 mL, 1.2 mol) were cocondensed with iron (11.19 g, 0.13 mol) over 3 h. Then a layer of ether was condensed in, and the mixture was allowed to warm slowly to −110 °C, where it was stirred for 20 min. It was then allowed to warm to room temperature. The mixture was filtered through a medium frit and then stripped to tacky solids on a vacuum line. The residue was extracted with pentane, filtered through Celite, and chromatographed on an alumina column to give a yellow-orange solution. This mixture was stripped to solids on a vacuum line, redissolved in a minimum of pentane, and cooled overnight to −40 °C to yield orange crystals from the red solution. These were collected under vacuum and washed with cold pentane, yield 10 g (10% based on evaporated iron).

Reaction of Iron with Cyclohexadiene and P(OMe)$_3$. Iron (12.0 g, 0.214 mol) and 1,3-cyclohexadiene (120 mL, 1.25 mol) were cocondensed over 1.75 h onto a liquid nitrogen cooled surface of pentane (40 mL). When this was complete, a layer of $P(OMe)_3$ (30 mL, 0.24 mol) was condensed in followed by a layer of pentane (60 mL). This was allowed to warm to −120 °C at which point it melted. It was then stirred as it warmed to room temperature. The suspension was filtered and volatiles were removed on a vacuum line. GC analysis of the volatiles showed benzene, cyclohexene, and 1,4-cyclohexadiene in addition to the compounds added to the mixture. The nonvolatile residue was extracted with pentane and filtered, and the extractions were concentrated before chromatography on alumina to remove a green and a brown band. The orange solution from chromatography was reduced in volume and cooled for 48 h at −40 °C giving orange solids which were collected by vacuum filtration at −40 °C. Sublimation at room temperature onto a liquid nitrogen cooled finger gave **49** (4.5 g). The unsublimed residue was recrystallized from pentane giving a yellow powder, **48** (4.5 g). The filtrate from the low-temperature filtration, a mixture of **32** and **50**, was separated by chromatography on silica gel. The red **50** was isolated in a 0.5-g yield and yellow **32** was isolated in 3.2-g yield.

The above reaction was repeated with 1,3-cyclohexadiene giving similar results.

Iron (8 g) was cocondensed with 1,3-cyclohexadiene (100 mL) and $P(OMe)_3$ (100 mL) over 2 h. Pentane was cocondensed into the reactor and the mixture was allowed to warm to −120 °C. The mixture was stirred for 1 h and then filtered. Volatiles were removed under vacuum and the residue was extracted with pentane. Chromatography in alumina gave a brown solution which was concentrated and cooled to −40 °C, precipitating brown-yellow solids. The solids (15 g) were mostly **32**, contaminated with **51** which was removed by recrystallization from pentane.

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Phenylseleno-[1] and Phenylsulfenolactonizations.[2] Two Highly Efficient and Synthetically Useful Cyclization Procedures

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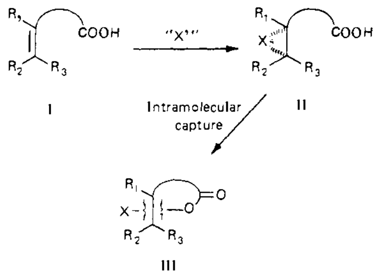
Abstract: Phenylselenolactonization and phenylsulfenolactonization, two new lactonization reactions, are described in detail. A series of unsaturated carboxylic acids was cyclized to phenylseleno- and phenylsulfenolactones by PhSeCl and PhSCl, respectively. These regio- and stereoselective ring closures are accompanied by the introduction into the organic structure of the synthetically useful PhSe and PhS groups and are, therefore, powerful synthetic methods. The phenylselenolactones so obtained are converted oxidatively with hydrogen peroxide and a variety of other oxidizing agents to unsaturated lactones and reductively to saturated lactones with Raney Ni or tri-*n*-butyltin hydride. The reversal of these cyclization reactions is effected with sodium in liquid ammonia. The mildness of the reactions described and their applicability to complex cases are demonstrated by the use of polyfunctional and sensitive substrates including prostanoid systems.

I. Introduction

Lactonization methodology plays an important role in modern organic synthetic chemistry not only because lactones occur in nature in great abundance and variety, but also because they constitute a particularly useful class of synthons. A major body of lactonizations involve the cyclization of open-chain hydroxy acids of which the most recent and elegant are the macrolide-forming reactions.[4] Another large category of lactonizations include those of unsaturated carboxylic acids (I) initiated by suitable electrophilic reagents. This latter class of ring closures, represented by eq 1 and proceeding by intramolecular capture of the reactive intermediate II, is a useful reaction in that not only does it form lactones (III) but also at the same time it offers selective functionalization of unsaturated substrates. In the past the initiation of these cyclizations of olefinic carboxylic acids has been carried out by acid,[5] lead tetraacetate,[6] mercuric reagents,[7] and halogens.[8] The most common and useful of these lactonizations, the halolactonization reaction, is a powerful process in organic synthesis for regio- and stereoselective functionalization of olefinic bonds even in acyclic systems.[9a] Its application to the stereocontrolled construction of complex natural products has been amply demonstrated.[9b,c] However, the usual requirement for aqueous basic media and the rather drastic conditions required to convert the halolactones to useful synthetic intermediates impose severe limitations to the scope of this method. The use of the other aforementioned lactonization procedures is even less widespread owing to the drastic conditions of the reactions



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