These results do not necessarily rule out some of the mechanisms suggested for the reactions mentioned in the Introduction, since NQR measures ground-state phenomena whereas the proposed mechanisms involve small-ring formation in a higher energy transition state. But these results might bear on questions of geometry of the transition state.

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Registry No. **2a**, 67951-82-0; **3g**, 67951-83-1; **4a**, 1043-49-8; **4b**, 941-77-5; **4c**, 30615-32-8; **4d**, 67951-73-9; **5a**, 21524-46-9; **5b**, 21571-80-2; **5c**, 21524-47-0; **5d**, 21524-51-6.

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Bis(diphenylphosphino)ethane Complexes of Iron

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The chemistry of a variety of bis(diphenylphosphino)ethane (DPPE) complexes of iron has been investigated. Zerovalent, five-coordinate complexes of iron have been prepared with CO and phosphorus ligands. Reactions with acetylenes give a series of hydrido acetylide complexes. Reaction with cyclopentadiene results in the loss of one DPPE to give Fe(DPPE)(Cp)H. Reactions with other compounds having activated C–H bonds give $\mathrm{Fe(DPPE)_2H_2}$. Reactions with tetracyanoethylene and tetracyanoquinodimethan involve electron transfer. Steric effects are shown to be important in determining the stability and geometry of the complexes.

Introduction

In a series of papers,[1-4] we have described the chemistry of $\mathrm{Fe(DMPE)_2H(C_{10}H_7)}$[5] (**1**). The studies included reactions with Lewis base ligands, L, such as phosphorus ligands, olefins, disubstituted acetylenes, and diazenes to give five-coordinate, zerovalent complexes, $\mathrm{Fe(DMPE)_2L}$, and the reaction with hydrogen to give $\mathrm{Fe(DMPE)_2H_2}$[2] (**2**). The cleavage reactions of C–H bonds involving hydrogen cyanide, monosubstituted

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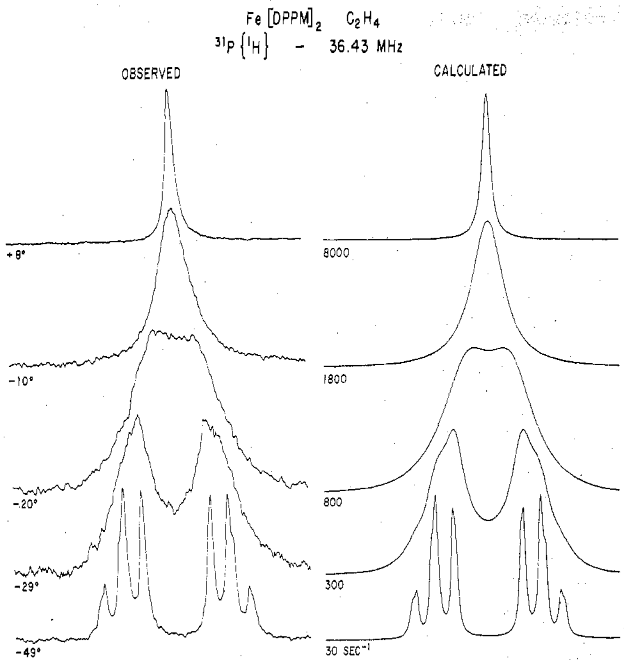
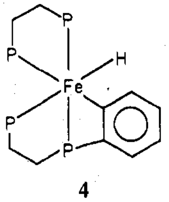


Figure 1. Observed and calculated $^{31}P\{^1H\}$ spectra of $Fe(DPPM)_2C_2H_4$ in toluene-d_8 as a function of temperature. Parameters used in the simulation are the following: $\delta_A = 28.3$, $\delta_B = 18.6$; $J_{AB} = 69$ Hz; $\Delta G^\ddagger = 11.4$ kcal/mol, $\Delta H^\ddagger = 11.6$ kcal/mol; $\Delta S^\ddagger = 0.7$ eu, at 25 °C.

acetylenes, and activated methyl and methylene compounds to give $Fe(DMPE)_2H(R)$ (R = cyanide, acetylide, CH_2X, and CHX_2, respectively) were described.[3] Finally[4] cleavage reactions of sp^2 C–H bonds such as those of olefins, arenes, and aldehydes were investigated. While the high basicity of **1** was responsible for the facile C–H bond cleavage reactions, steric effects played a dominant role in the determination of product distributions and stereochemistry.

A variety of iron complexes involving the aryl-substituted, bidentate phosphorus ligand DPPE[5] have been reported. The complex $Fe(DPPE)_2(C_2H_4)$ (**3**) has been prepared by triethylaluminum reduction of $Fe(acac)_3$ in the presence of DPPE,[6] a reaction later shown to proceed through the intermediate Fe(DPPE) $(acac)_2$.[7] Subsequent photolysis of **3** led to the ortho-metalated product **4**. When the aluminum alkyl reduction was carried out with trimethylaluminum, $Fe(DPPE)_2Me_2$ was isolated.[8] Stepwise, borohydride reduction of $FeCl_2$ in the presence of DPPE yielded *trans*-$Fe(DPPE)_2HCl$[9] (**5**) and *cis*-$Fe(DPPE)_2H_2$[10] (**6**).



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These complexes present logical starting points for a systematic investigation of reactions similar to those carried out with **1**. The results of that investigation are presented here.

Results and Discussion

Preparation and Characterization of the Starting Materials. The complex $Fe(DPPM)_2(C_2H_4)$[5] (**7**) was prepared by triethylaluminum reduction in a manner analogous[6] to that reported for **3**. When preparation of $Fe(DPPP)_2(C_2H_4)$[5] was attempted in a similar manner, the product did not precipitate as in the two previous cases and attempted workup yielded only uncharacterizable red oils. The $^{31}P\{^1H\}$ NMR spectrum of **3** from room temperature up to its decomposition point is an apparent A_2B_2 spin system indicating a stereochemically rigid molecule. In contrast, the spectrum of **7** varies with temperature as shown in Figure 1. The reduced steric bulk of the DPPM ligand is the most likely factor which leads to a lower barrier for the intramolecular exchange process responsible for equilibration of the four phosphorus nuclei. For comparison, the complex $Fe(DMPE)_2(C_2H_4)$ is fluxional at room temperature and frozen out at −25 °C.

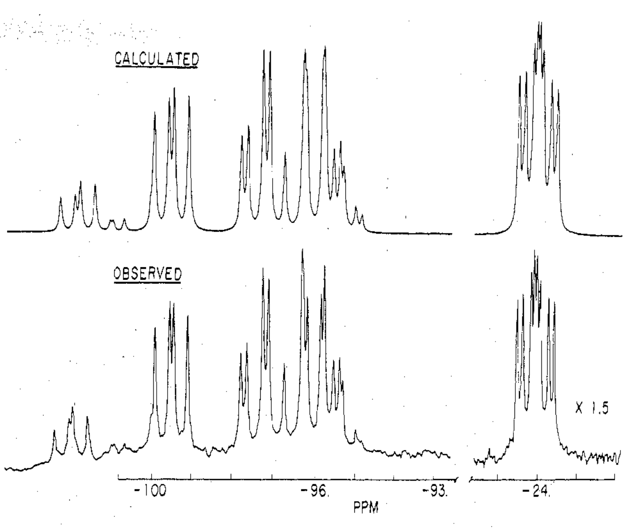
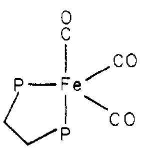


Figure 2. Observed and calculated $^{31}P\{^1H\}$ (36.43 MHz) spectra of $Fe(DPPE)H(C_6H_4PhPC_2H_4PPh_2)$ in toluene-d_8 at 25 °C. Parameters used in the simulated spectrum are the following: $\delta_A = 23.7$, $\delta_B = 95.2$, $\delta_C = 96.1$, $\delta_D = 101.3$; $J_{AB} = 23$, $J_{AC} = 6.5$, $J_{AD} = 19$, $J_{BC} = 29$, $J_{BD} = 18$, $J_{CD} = 111$ Hz.

Attempts to prepare the propylene or isobutylene analogues of **3** using $AlPr_3$ or $Al(i\text{-}Bu)_3$ were unsuccessful, giving instead *cis*-$Fe(DPPE)_2H_2$ (**6**) (not the trans isomer as reported earlier[8]). This product is not the previously reported[10] yellow material isolated from borohydride reduction of $FeCl_2$ in the presence of DPPE but instead is dark red. As reported elsewhere,[8] the yellow isomer of the dihydride, **6Y**, is easily converted to this red isomer, **6R**, by exposure to visible light. Conversely, the red isomer is converted to the yellow one by recrystallization from a variety of solvents. These two compounds are spectroscopically indistiguishable in solution so that the difference in color can presumably be attributed to a solid-state effect. A change in phenyl ring conformation causes similar color changes in another system.[11] Observation of analogous light sensitivity for zerovalent nickel DPPE complexes[12] also supports a mechanism of this type.

The conversion of **3** to **4** has been reported[6] to occur by photolysis or heating in the presence of some of the "mother liquor" left over from the preparation of **3**. We find both techniques to be unnecessary; simple refluxing in toluene causes loss of ethylene and ortho metalation. The $^{31}P\{^1H\}$ NMR spectrum of **4** consists of an ABCD spin system; the calculated and observed spectra are shown in Figure 2. There is a marked high field shift of the resonance assigned to the phosphorus atom bearing the metalated ring. This is in accord with the observation that three- and four-membered rings give upfield ^{31}P chemical shifts while five-membered rings give downfield shifts[13] relative to electronically similar monodentate ligands.

Reactions with Lewis Base Ligands. Reaction of **3** with excess CO for 3 days gives a mixture of $Fe(DPPE)_2CO$ (**8**) and $Fe(DPPE)(CO)_3$ (**9**) (assigned by CO stretching frequencies of 1834 cm^{-1} and 1978, 1910, and 1891 cm^{-1}, respectively[14]). The ^{31}P NMR spectra of both **8** and **9** remained as sharp single lines on cooling to −80 °C, indicating fast intramolecular exchange of the phosphorus nuclei. There was no evidence for formation of an appreciable concentration



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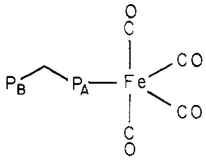
of $Fe(DPPE)_2(CO)_2$ as reported elsewhere.[8]

The dihydride **6R** reacts with CO more slowly but ultimately gives both **8** and **9**. In addition, two other bands were observed in the infrared spectrum at 2045 and 1935 cm^{-1} and may indicate a hydrido carbonyl species. There was no observed reaction of **5** with CO under similar conditions. Carbon monoxide reacted cleanly with **4** in a short period of time giving **8** which could be isolated or reacted further to give **9**.

When **7** reacted with CO, the complexes $Fe(DPPM)_2CO$ (**10**) (ν_{CO} 1836 cm^{-1}) and $Fe(DPPM)(CO)_3$ (**11**) (ν_{CO} 1977, 1908, and 1897 cm^{-1}) analogous to **8** and **9** were observed. Another complex, formulated as $Fe(DPPM)(CO)_4$ (**12**), was also observed (ν_{CO} 2044 cm^{-1}). (Other bands may have been hidden under those above.) This unusual complex gave rise to $^{31}P\{^1H\}$ resonance at $\delta_A = +74.5$[15] and $\delta_B = -27.2$ with a coupling of $J_{AB} = 25$ Hz and is assigned structure **12**. The low carbonyl stretching frequencies of these complexes relative to some other complexes (Table I) indicate a high degree of electron density on the metal centers. The frequency observed for $Fe(DMPE)_2CO$ was lower still.[2]



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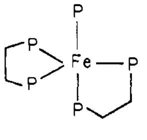
A similar pattern of reactivity was observed with PF_3. Reactions with **3** and **6** were slow enough for appreciable formation of $Fe(DPPE)(PF_3)_3$ (**13**) before the starting material converted completely to $Fe(DPPE)_2(PF_3)$ (**14**). Reaction of PF_3 with **4** gave **14** cleanly in minutes at room temperature.

Reaction of phosphorus ligands, P, with **4** was the route of choice for preparing complexes of the type $Fe(DPPE)_2P$.[16] Other compounds (**15–21**) prepared by the technique are listed in Table II in order of increasing cone angle of P.[17] No reaction was observed with phosphorus ligands having cone angles greater than 116°, including PMe_3, PMe_2Ph, and $P(OPh)_3$. This can be compared to the preparation of $Fe(DMPE)_2P$ complexes with P having cone angles up to 141° ($P(O\text{-}o\text{-}Tol)_3$).[2] The steric constraints of the $Fe(DPPE)_2$ system are much more severe than those of the $Fe(DMPE)_2$ system.

Steric effects also play an important role in the stereochemistry of the complexes. All $Fe(DPPE)_2P$ complexes are stereochemically nonrigid at room temperature, resulting in ^{31}P NMR spectra consisting of AB_4 spin systems. The sparing solubility of the complexes and the very complicated nature of their spectra in slow exchange put a detailed investigation of the exchange process beyond the scope of this work, but the slow-exchange limiting spectra display an interesting AB_2CD spin system (Figure 3), assigned to the structure



Our previous work[18] demonstrated that the preferred geometry for zerovalent iron complexes having five monodentate phosphorus ligands is a trigonal bipyramid. The apical positions are more sterically encumbered than the equatorial positions so that it is not surprising that the smaller ligand would occupy this site (the cone angle of half of DPPE is 125°).[17] This geometry does require that one of the DPPE ligands, which has a bite angle of 85°, span an equatorial–equatorial angle, normally 120°, but this phenomenon of angle contraction has been observed in other systems.[19]

Table I. Carbonyl Stretching Frequencies of Selected Complexes[a]

$Fe(DPPE)_2CO$	1834
$Fe(DPPE)(CO)_3$	1978, 1910, 1891
$Fe(DPPM)_2CO$	1836
$Fe(DPPM)(CO)_3$	1977, 1908, 1897
$Fe(DPPM)(CO)_4$	2044
$Fe(DMPE)_2CO$	1812
$Ru(DMPE)_2CO$	1830
$Ni(PMe_3)_3CO$	1900
$Ni(P(OMe)_3)_3CO$	1952
$Fe(P(OMe)_3)_4CO$	1864

[a] cm^{-1}, measured in toluene.

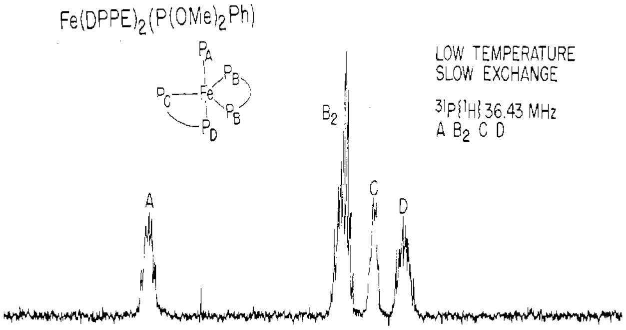
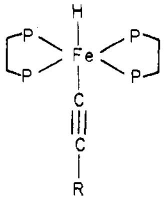


Figure 3. $^{31}P\{^1H\}$ spectrum of $Fe(DPPE)_2(P(OMe)_2Ph)$ at the slow-exchange limit (−80 °C) displaying the AB_2CD spin system which is typical of the $Fe(DPPE)_2$(phosphorus ligand) complexes.

Cleavage of Carbon–Hydrogen Bonds. Monosubstituted acetylenes react readily with **3** and **4**, and more slowly with **6**, to form hydrido acetylide complexes **22–26** similar to those observed in reactions with **1**[3] and $Fe(DPPE)_2Me_2$.[8] The rate of reaction is very dependent on the nature of the substituent. As an example the reactions of **3** with *tert*-butyl-, phenyl-, trifluoromethyl-, and carboethoxyacetylenes took days, hours, minutes, and seconds, respectively. The products were all trans isomers. When the reactions were followed by $^{31}P\{^1H\}$ NMR, no cis intermediates were observed. Reaction of DC≡CPh with **3** and **4** gave deuterium only in the hydrido position with no incorporation into the DPPE for **4**. When DC≡CPh reacted with **6** an appreciable portion of the complex contained no deuterium. The unreacted portion of **6** also contained no deuterium so there was no deuterium scrambling before the addition took place. It therefore seems that oxidative addition of the acetylene precedes reductive elimination of hydrogen so that H–D scrambling takes place in the reaction intermediate. The phosphite addition reactions had already indicated that reductive elimination of the ortho metalated phenyl from **4** is more facile than either loss of ethylene from



22, R = *t*-Bu
23, R = Ph
24, R = CF_3
25, R = CO_2Et
26, R = COMe

Table II. $^{31}P\{^1H\}$NMR Parameters

		spin system	δ_A[a]	δ_B[a]	J_{AB}[b]
	DPPE	A_2	−13.4		
	DPPM	A_2	−22.2		
3	$Fe(DPPE)_2(C_2H_4)$	A_2B_2	94.5	78.1	40
4	$Fe(DPPE)H(C_6H_4P(Ph)C_2H_4PPh_2)$	ABCD	*e*	*e*	*e*
5	$Fe(DPPE)_2HCl$	A_4	81.5		
6	$Fe(DPPE)_2H_2$	A_2B_2	102.9	90.3	19 (at 25 °C)
7	$Fe(DPPM)_2(C_2H_4)$	A_2B_2	28.4	18.6	62
8	$Fe(DPPE)_2CO$	A_4	96.3		
9	$Fe(DPPE)(CO)_3$	A_2	95.8		
10	$Fe(DPPM)_2(CO)$	A_4	20.7		
11	$Fe(DPPM)(CO)_3$	A_2	19.4		
12	$Fe(DPPM)(CO)_4$	AB	74.5	−27.2	25
13	$Fe(DPPE)(PF_3)_3$	$(AX_3)_3B_2$	158	92.1	broad
14	$Fe(DPPE)_2(PF_3)$	$(AX_3)B_4$	134.3	89.8	8
15	$Fe(DPPE)_2(P(OCH_2)_3CEt)$	AB_4	140.6	90.5	8
16	$Fe(DPPE)_2(P(OMe)_3)$	AB_4	155.2	86.9	10
17	$Fe(DPPE)_2(P(OEt)_3)$	AB_4	152.2	86.4	10
18	$Fe(DPPE)_2(P(OBu)_3)$	AB_4	156.0	86.3	11
19	$Fe(DPPE)_2(P(OMe)_2Ph)$	AB_4	173.1	86.9	7
20	$Fe(DPPM)(PF_3)_3$	$(AX_3)_3B_2$	162.	14.5	broad
21	$Fe(DPPM)(P(OMe)_3)_3$	A_3B_2	179.	20.	11
22	$Fe(DPPE)_2H(C{\equiv}C\text{-}t\text{-}Bu)$	A_4X	89.21	16.42[c]	(45)[d]
23	$Fe(DPPE)_2H(C{\equiv}CPh)$	A_4X	89.0	16.32[c]	(45.5)[d]
24	$Fe(DPPE)_2H(C{\equiv}CCF_3)$	A_4X	88.91	14.54[c]	(46)[d]
25	$Fe(DPPE)_2H(C{\equiv}CCO_2Et)$	A_4X	89.0	13.87[c]	(45)[d]
26	$Fe(DPPE)_2H(C{\equiv}CCOMe)$	A_4X	89.0	13.48[c]	(44.5)[d]
27	$Fe(DPPE)_2H(CN)$	A_4X	90.10	13.07[c]	(44)[d]
28	$Fe(DPPE)_2CN_2$	A_4	91		
29	$Fe(DPPE)H(Cp)$	A_2X	110.8	16.12[c]	(72)[d]

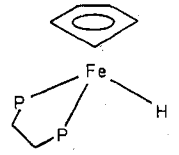
[a] In ppm; positive is downfield of 85% H_3PO_4. Recorded in toluene. [b] In Hz. [c] ^1H NMR hydride chemical shift, ppm above Me_4Si. [d] Hydride J_{PH} in Hz. [e] See Figure 2.

3 or reductive elimination of H_2 from **6**. This would explain the lack of total deuterium incorporation in reactions with **6**.

The reaction of HCN with **3** gives $Fe(DPPE)_2H(CN)$ (**27**), the analogue of the acetylides. If excess HCN is used, a second product, $Fe(DPPE)_2(CN)_2$ (**28**), is also isolated. The fate of the hydrogen produced in the reaction has not been determined.

We have shown elsewhere[1,3] that **1** reacts with compounds having activated methyl groups to yield hydrido complexes bearing coordinated substituted methyl groups. Complexes in the $Fe(DPPE)_2$ system were investigated for similar behavior. Compounds **3**, **4**, and **6** dissolve in solvents such as acetone and acetonitrile with no reaction. Reactions of **3** and **4** are observed in the more highly activated systems, diethyl malonate and malononitrile, but the only characterizable products from these reactions were **6** and DPPE. The reaction presumably follows a course similar to that observed[7] in the reaction of β-diketones with **3**. The diketone reactions involve C–H bond cleavage at the methylene followed by a disproportionation to yield equimolar quantities of **6**, Fe(DPPE)(β-diketonate)$_2$, and DPPE. In the present system, the added stability from chelation is not available and the adduct decomposes.

The reaction of cyclopentadiene with **1** gave $Fe(DMPE)_2H(C_5H_5)$ in which the cyclopentadienyl group is η^1 and nonfluxional.[4] Reaction of cyclopentadiene with **3** gives the known[20] complex, **29**, in which one DPPE has been lost



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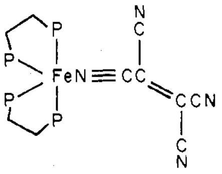
and the cyclopentadienyl ring is η^5. The cyclopentadienyl ^1H resonance is observed as a singlet at 4.13 ppm and the hydride as a triplet at −16.12 ppm (J_{PH} = 72 Hz).

Nitromethane provides a highly activated methyl group for C–H bond cleavage reactions but on mixing with **1** the only reaction observed was ligand oxidation yielding oxides of DMPE. Reaction of nitromethane with **3** is rapid but the only product isolated was free DPPE. In this system, oxidation again takes place but, unlike the $Fe(DMPE)_2$ system, the metal rather than the ligands is oxidized.

Reactions Involving Electron Transfer. Attempts to prepare olefin complexes with simple olefins other than the ethylene in complex **3** were unsuccessful. We expected[21] that the bonding of TCNE to an electron-rich system such as zerovalent iron should result in a complex significantly more stable than an ethylene complex. The reaction of TCNE with **3** in THF at room temperature gave a marked color change, going from an orange-vermilion suspension to a yellow-olive suspension upon mixing. One equivalent of ethylene was liberated by the reaction. The resultant, sparingly soluble complex has a solid-state IR spectrum (Nujol) displaying bands at 2183, 2175, 2145, and 2095 cm^{-1}. A similar pattern of bands (2211, 2192, 2152, and 2098 cm^{-1}) has been reported[22] for N-bonded TCNE in $V(Cp)_2Br(TCNE)$ which has been characterized crystallographically. Thus the adduct probably has structure **30**. The NMR spectra of this complex could not be obtained, presumably due to its sparing solubility and the presence of paramagnetic impurities; very dilute solutions displayed the characteristic ESR spectra of the TCNE radical anion.[23]



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In order to obtain more information about the reaction mechanism and to assess the role of the TCNE radical anion in this reaction, a more careful ESR study was carried out.

Table III. Analytical Data and Melting Points

			% C		% H		% P		% other		
		mp, °C	calcd	obsd	calcd	obsd	calcd	obsd	element	calcd	obsd
3	$Fe(DPPE)_2(C_2H_4)$	165-166	73.6	72.7	5.95	5.71	14.1	15.1	Fe	6.3	7.6
4	$Fe(DPPE)H(C_6H_4P(Ph)C_2H_4PPh_2)$	179-180	73.2	72.7	5.67	5.70	14.5	15.1	Fe	6.6	7.7
5	$Fe(DPPE)_2HCl$	195	70.2	70.2	5.55	5.79	13.9	14.3	Cl	4.0	3.7
6	$Fe(DPPE)_2H_2$	230-231	73.1	73.3	5.90	5.87	14.5	14.0			
7	$Fe(DPPM)_2(C_2H_4)$	165	73.2	73.7	5.71	5.90	14.5	15.2			
14	$Fe(DPPE)_2(PF_3)$	225-230	66.4	64.1	4.14	4.28	16.5	16.4	F	6.06	6.01
15	$Fe(DPPE)_2(P(OCH_2)_3CEt)$	133-134	68.7	68.3	5.87	6.17	15.3	15.1	O	5.7	4.7
16	$Fe(DPPE)_2(P(OMe)_3)$	144-147	67.6	67.4	5.89	5.91	15.9	16.9	O	4.9	5.1
17	$Fe(DPPE)_2(P(OEt)_3)$	175	68.4	68.1	6.23	6.18	15.2	15.9	O	4.7	4.6
18	$Fe(DPPE)_2(P(OBu)_3)$	134-136	69.7	68.6	6.87	6.79	14.0	14.5	O	4.4	5.1
19	$Fe(DPPE)_2(P(OMe)_2Ph)$	136-138	70.7	70.7	5.55	6.02	15.2	15.5	O	3.1	2.7
22	$Fe(DPPE)_2H(C{\equiv}C\text{-}t\text{-}Bu)$	209	74.5	74.3	6.25	6.21	13.3	13.7			
23	$Fe(DPPE)_2H(C{\equiv}CPh)$	209-210	75.5	75.5	5.70	5.75	13.0	11.3			
24	$Fe(DPPE)_2H(C{\equiv}CCF_3)$	269-270	69.8	69.7	5.22	5.34	13.1	13.4	F	6.0	5.6
25	$Fe(DPPE)_2H(C{\equiv}CCO_2Et)$	185 dec	72.0	72.4	5.73	5.77	13.03	12.1			
26	$Fe(DPPE)_2H(C{\equiv}CCOMe)$	156 dec	73.1	72.5	5.69	5.95	13.5	13.0			
27	$Fe(DPPE)_2H(CN)$	170 dec	72.4	72.8	5.61	5.68	14.1	13.7	N	1.59	1.81
28	$Fe(DPPE)_2(CN)_2$	>300	71.7	72.0	5.35	5.61	13.7	11.7	N	3.10	3.22
29	$Fe(DPPE)H(Cp)$		71.6	71.3	5.8	5.7	11.9	12.2			
30	$Fe(DPPE)_2TCNE$	205 dec	71.0	70.6	4.9	5.4	12.6	13.2	N	5.7	5.8
31	$Fe(DPPE)_2(TCNE)_2$	220 dec	69.3	68.6	4.36	4.43	11.2	10.1	N	10.1	10.0

Upon mixing a 0.5×10^{-3} M THF solution of **3**, cooled to −78 °C, with an equal volume of an equimolar THF solution of TCNE at the same temperature, the orange-vermilion of **3** changes instantaneously to light yellow which persists indefinitely provided the temperature of the mixture is not allowed to rise above −78 °C. At this temperature, the ESR spectrum of the solution consisted on two signals: the characteristic narrow-line spectrum of the TCNE radical anion superimposed on a very broad single absorption curve. Because of the widely different line widths in solution, the presence of two paramagnetic species in comparable amounts became clearer by freezing the sample at −160 °C. At this temperature, the organometallic paramagnetic species displays a structureless isotropic absorption with a *g* factor of 2.047 and a line width of about 70 G. If the yellow sample is warmed briefly to room temperature, its color changes rapidly to deep green. This solution, under instrumental conditions strictly comparable to those employed for the initial spectrum at −78 °C, displayed, at the latter temperature, a spectrum of the TCNE radical reduced in intensity by a factor of about 100. Examination of the sample at −160 °C gave no evidence of paramagnetic iron-containing species. The formation of the TCNE radical anion in the reaction of **3** with TCNE at −78 °C is essentially stoichiometric as established by comparison of the ESR intensities using a 0.25×10^{-3} M THF solution of highly purified $K^+[TCNE]^{-}\cdot$ under strictly comparable conditions. The above results demonstrate that the initial step in the reaction is a single electron transfer from **3** to TCNE with the formation of the 17-electron radical cation of **3** which is thermally very unstable toward loss of ethylene. After loss of ethylene, a further rapid reaction between the resultant 15-electron cation and $TCNE^{-}\cdot$ leads to the 18-electron complex **30**. The latter reaction may be reversible to some extent which would explain the observation of the TCNE radical anion in solutions of **30**. More probably, however, in view of the high sensitivity of the ESR technique and the difficulty in preparing highly pure **30** due to its low solubility in common solvents, the observation of trace amounts of $TCNE^{-}\cdot$ may be related to minor side reactions.

Single electron transfer to an electron acceptor is thus a viable reaction path for organometallic complexes with several phosphorus ligands which are relatively electron rich at the metal center.[24–27] Salts of the radical cations $Fe(CO)_3L_2^{+}\cdot$ (L = phosphines, phosphites; L_2 = DPPE) have been isolated and studied by ESR.[24] Their *g* factors are in the range of 2.05 and are thus comparable to the *g* factor of the unstable $\mathbf{3}^{+}\cdot$. The line width of $\mathbf{3}^{+}\cdot$ is also consistent with unresolved hyperfine structure due to four phosphorus nuclei.[24] The highly electron-rich $Fe[P(OMe)_3]_5$ also undergoes facile electron-transfer reactions with TCNE and even with the active alkyl halides such as chlorofluorocarbons[27] and allyl bromide.

Reaction of **30** with another equivalent of TCNE or reaction of **3** with 2 equiv of TCNE gives a very intensely colored deep blue-green compound, **31**, which in contrast to **30** is very soluble in THF. The solid-state (Nujol) infrared spectrum of **31** displays three rather broad bands at 2253, 2185, and 2141 cm^{-1}. The ESR spectrum displayed only the signal of $TCNE^{-}\cdot$ and its intensity is roughly equivalent to that expected for half of the TCNE in the system. Thus **31** is formulated as $[Fe(DPPE)_2TCNE]^{+}\cdot[TCNE]^{-}\cdot$.

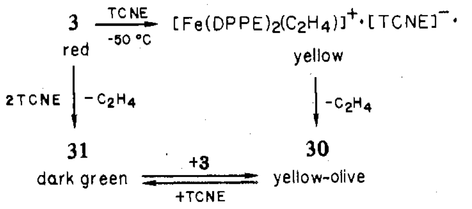
These observations can be rationalized by Scheme I. Similar reactions with similar color changes using TCNQ give the $TCNQ^{-}\cdot$ radical anion. Mixed experiments involving both TCNE and TCNQ gave spectra too complicated to interpret.

The reaction of 1 equiv of TCNE with **4**, **6**, or $Fe(DPPE)_2(Me)_2$ (**32**) also yields **30**. With **4**, no gas is evolved from the reaction but the ortho-metalated DPPE phenyl group undergoes reductive elimination. Reaction with **6** or **32** evolves 1 equiv of H_2 or C_2H_6 (with a trace of CH_4), respectively. Presumably in all three cases, the Fe(II) species are first oxidized to Fe(III) and then undergo reductive elimination of C–H, H–H, or C–C, lowering the formal oxidation state to Fe(I). The oxidation of **32** with I_2 in benzene liberates CH_4 and C_2H_6 in the ratio of 1:2.5.[8] It is possible that the proportion of ethane would have been increased if the oxidation had been carried out more quickly. The reaction of TCNE with $Ru(PPh_3)_4H_2$ gives $Ru(PPh_3)_2(TCNE)_3$[28] but the mode of coordination was not discussed. Oxidation of methylgold species also gives ethane.[29]

Experimental Section

All manipulations were carried out in a dry nitrogen atmosphere. All phosphorus ligands are commercially available, as are the iron starting materials. All solvents were dried by standard techniques. Melting points were measured under vacuum and are uncorrected. The ^{31}P NMR spectra were recorded using a Bruker HFX-90 spectrometer (at 36.43 MHz). Proton spectra were recorded using Varian HR-220 and XL-100 spectrometers. Analyses were carried out at our analytical facilities. Compounds **5**[9] and **6Y**[10] were prepared by literature methods. Analyses and melting points are presented in Table III.

Scheme I



Preparation of $Fe(DPPE)_2(C_2H_4)$ (3). A suspension of $Fe(acac)_3$ (42.4 g, 120 mmol) and DPPE (95.2 g, 240 mmol) in ether (400 mL) is reacted with $AlEt_3$ (119 mL, 800 mmol) in ether (100 mL) over 45 min. It is critical to maintain a temperature of −15 to −5 °C during this step. Above 0 °C the product will be contaminated with $Al(acac)_3$, and below −20 °C the formation of $Fe(DPPE)_2H_2$ is favored. The initial red-orange color turns to a golden brown and eventually to a brick red. Stirring is continued at least 3 h (often overnight). The product is collected by vacuum filtration and washed repeatedly with ether to remove any $Fe(DPPE)_2H_2$ or free DPPE; yield 85 g (80%), mp 165–166 °C. The use of $AlEt_2(OEt)$ for the reduction makes control of temperature much less critical.

Preparation of $Fe(DPPE)H[(C_6H_4)PhPC_2H_4PPh_2]$ (4). It has been reported[6] that photochemical activation is necessary to prepare the hooked hydride species from the ethylene complex prepared in the preceding synthesis. While this method can be used, the thermal reaction goes nicely in refluxing toluene with evolution of ethylene. The entire yield from the preceding preparation is dissolved in 500 mL of toluene at elevated temperature. The solution is brought to reflux for 10 min and then cooled. Addition of pentane causes an orange-red precipitate to form. The product is collected by vacuum filtration and washed with ether. Recrystallization from ether gives a product having a melting point of 179–180 °C.

Preparation of Red $Fe(DPPE)_2H_2$ (6R). This complex was prepared in a manner analogous to that used for 3, substituting $Al(i\text{-}Bu)_3$ instead of $AlEt_3$. The reaction is run at −78 °C giving a very dark oily mixture from which the desired product precipitates as the mixture warms to room temperature. The dark red crystalline material is washed with ether and pentane and dried under vacuum; yield 85%.

Preparation of $Fe(DPPM)_2C_2H_4$ (7). This compound was prepared in the same manner as $Fe(DPPE)_2C_2H_4$ (3) but on a smaller scale.

Reactions with CO. Reactions with CO were carried out in a thick-walled 4 × 1 in. glass tube connected by an O-ring seal to a pressure gauge and needle valve. The tube was evacuated to remove N_2 and charged with CO to a pressure of 15 psig. Small samples were removed periodically for $^{31}P\{^1H\}$ NMR, ^1H NMR, and infrared spectroscopy. The products were not isolated.

Preparation of $Fe(DPPE)_2(PF_3)$ (14). A toluene (20 mL) suspension of 4 was reacted with PF_3 (70 mL, 3.0 mmol) at room temperature. The suspension turned to a dark red solution in about 5 min before an orange product began to precipitate. After stirring an additional 20 min, the orange powder was collected by vacuum filtration and washed with several portions of ether.

Preparation of $Fe(DPPE)_2[P(OMe)_3]$. Toluene solutions of 4 (2.56 g, 3.0 mmol) and $P(OMe)_3$ (slight excess) were reacted at room temperature. An orange-brown precipitate formed. The solution was reduced in volume under vacuum, precipitating more solids which were collected by vacuum filtration. The product was washed with ether and pentane before drying under vacuum. The product was then recrystallized from toluene/ether. Other compounds prepared in this manner are $Fe(DPPE)_2[P(OCH_2)_3CEt]$ (15), $Fe(DPPE)_2[P(OEt)_3]$ (17), $Fe(DPPE)_2[P(OBu)_3]$ (18), and $Fe(DPPE)_2[P(OMe)_2Ph]$ (19).

The properties of these complexes are given in Table II. The ^{31}P data are for the high-temperature fast-exchange limit where the spectra can be analyzed as AB_4 spin systems. As the temperature is lowered, the spectra become more complex as the exchange is frozen out. At the slow-exchange limit the spectra are AB_2CD spin systems. The spectrum of $Fe(DPPE)_2[P(OMe)_2Ph]$ is shown as an example (Figure 3).

Preparation of $Fe(DPPE)_2H(C{\equiv}CPh)$ (23). A solution of $Fe(DPPE)_2C_2H_4$ (2.64 g, 3.0 mmol) in THF (30 mL) was treated with an excess of phenylacetylene (1.5 mL). The red-orange suspension turned to a dark red solution over a period of several hours. Stirring was continued for 24 h before the solution was filtered through Celite. The filtrate was stripped to dryness and the solids were suspended in ether. Vacuum filtration give golden solids which were washed with ether and dried under vacuum; yield 70%.

The other acetylide complexes (22–26) were prepared similarly. The major variable was reaction time as noted in the discussion.

The hydrido cyanide complex, 27, was prepared similarly, using only 1 equiv of HCN. With an excess of HCN the very insoluble complex 28 was obtained directly from the suspension.

Preparation of Fe(DPPE)H(Cp) (29). A solution of $Fe(DPPE)_2C_2H_4$ (2.64 g, 3.0 mmol) in THF (40 mL) was treated with a large excess of freshly cracked cyclopentadiene. There was no immediate reaction and the mixture was allowed to stir for 1 week. All of the product went into solution. The mixture was filtered and stripped to dryness. Suspension in ether and filtration gave impure DPPE which was removed by vacuum filtration. The filtrate was stripped to dryness giving an orange precipitate. Recrystalization from ether gave 29 in 50% yield.

Preparation of $Fe(DPPE)_2TCNE$ (30). A solution of $Fe(DPPE)_2(C_2H_4)$ (2.64 g, 3.0 mmol) in THF (24 mL) was reacted with a solution of TCNE (0.38 g, 3.0 mmol) in THF. The red-orange solution turned emerald green (evolution of 2.8 mmol of C_2H_4). The solution was filtered, and addition of ether caused precipitation of a green microcrystalline product. This reaction can be carried out equally well starting with $Fe(DPPE)_2H_2$ and evolving 1 equiv of H_2; yield 90%.

Preparation of $Fe(DPPE)_2(TCNE)_2$ (31). The preceding reaction was carried out in acetonitrile using 0.76 g of TCNE. As the second equivalent of TCNE was added, the solution went from the initial green color to a very intense black-green. The volume was reduced and the product was precipitated by very slow addition of ether. (Rapid addition results in formation of an oil.) The dark green-black material was collected by vacuum filtration and dried under vacuum; yield 90%.

Registry No. **3**, 36222-39-6; **4**, 19392-92-8; **5**, 19392-93-9; **6**, 32490-69-0; **7**, 62648-49-1; **8**, 60105-56-8; **9**, 14881-58-4; **10**, 67827-26-3; **11**, 41685-05-6; **12**, 52843-12-6; **13**, 67827-27-4; **14**, 67827-28-5; **15**, 67827-29-6; **16**, 62613-13-2; **17**, 67827-30-9; **18**, 67827-31-0; **19**, 67827-17-2; **20**, 67827-18-3; **21**, 62572-56-9; **22**, 67827-19-4; **23**, 67889-80-9; **24**, 67827-20-7; **25**, 67827-21-8; **26**, 67827-22-9; **27**, 67827-23-0; **28**, 67827-24-1; **29**, 51509-20-7; **30**, 67827-25-2; **31**, 67904-74-9.

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Coordination Chemistry of Bidentate Difluorophosphines. 3. Complexes of 1,2-Bis(difluorophosphino)cyclohexane with Molybdenum(0), Manganese(I), and Iron(0)[1]

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1,2-Bis(difluorophosphino)cyclohexane, $F_2PC_6H_{10}PF_2$ (L), has been found to react with pentacarbonyliron(0), $Fe(CO)_5$, and with pentacarbonylmanganese(I) bromide, $Mn(CO)_5Br$, in hexane, displacing 2 mol of carbon monoxide/mol of ligand. The resulting products, $LFe(CO)_3$, $L_2Fe(CO)$, $LMn(CO)_3Br$, and $L_2Mn(CO)Br$, are all air-stable solid monomers indicating that L is an effective chelating agent. A slight excess of L also reacts readily with bis(toluene)molybdenum(0) displacing the toluene to give L_3Mo, also an air-stable monomer. This result contrasts with the formation of bridged species on reaction of L with $Mo(CO)_6$ and the other 6B metal hexacarbonyls. All new compounds were characterized by elemental analysis and osmometric molar mass and by IR, NMR, and mass spectra. Analysis of the IR and NMR data supports the conclusion that L functions as a strong π acceptor and assists in assigning structures.

We have recently presented evidence that *trans*-1,2-bis(difluorophosphino)cyclohexane functions as an unusually strong π acceptor in its complexes with the group 6B metals[2a] and with Ni.[2b] It functions as a bidentate and/or as a bridging bifunctional ligand in these compounds. Analysis of the Cotton–Kraihanzel CO force constants[3] and NMR parameters resulted in assignment of π acidity comparable to that of PCl_3 and slightly greater than that of $CH_3N(PF_2)_2$. The latter is the only other bidentate, strong π-acid ligand to have received substantial attention.[4-8] Both of these ligands are of interest because the chelate effect is expected to render their complexes with metals in low oxidation states even more stable than can monodentates such as CO. One noteworthy contrast between these two ligands is the nature of the reaction products resulting from photoreaction with the group 6B metal carbonyls. While $CH_3N(PF_2)_2$ readily displaces the CO to give chelates,[4] $F_2PC_6H_{10}PF_2$ gives bridged complexes[2a] though it chelates readily with Ni(0). In order to characterize further the coordinating behavior of $F_2PC_6H_{10}PF_2$ we have studied its reactions with metals having different stereochemical demands, specifically with Mn(I) and Fe(0). In addition, we report evidence that the formation of bridged complexes of Mo(0) observed previously is not indicative of an inability of this ligand to form chelates about a six-coordinate metal.

Experimental Section

General Techniques. Standard high-vacuum techniques were employed throughout[9], and manipulations of the reaction products were carried out under dry nitrogen. Infrared spectra of the complexes in hexane and chloroform were recorded on a Beckman IR-20A spectrometer. Values reported are correct to ±3 cm^{-1}. Proton NMR spectra were obtained at 60 MHz with a Varian Associates EM-360 instrument. ^{19}F NMR spectra were obtained at 94.1 MHz with a Varian Associates XL-100-12 instrument. ^{31}P NMR spectra were obtained at 40.5 MHz with a Varian Associates XLFT-100-15 instrument in the Fourier transform mode with proton noise decoupling and a deuterium lock. The ^{13}C NMR spectrum was obtained at 25.2 MHz with a Varian Associates XLFT-100-15 instrument in the Fourier transfer mode with fluorine noise decoupling and a deuterium lock. Chemical shift values are given in ppm from benzene (internal standard), CCl_3F and 85% orthophosphoric acid (external standards), and Me_4Si (corrected from $CDCl_3$, $\delta_{Me_4Si} = \delta_{CDCl_3} + 77$), respectively. (Chemical shifts are given as + = downfield.) Mass spectra were obtained at 70 eV with an Hitachi Perkin-Elmer RMU-6E spectrometer applying a solid inlet system. Molecular weights were determined osmometrically in benzene or chloroform with a Mechrolab vapor pressure osmometer, Model 301A. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. A Rayonet photochemical reactor (Southern NE Ultraviolet Co., Middleton, Conn.) containing RPR-3000 A reactor lamps was used as the energy source for the photoreactions.

Materials. All organic solvents were dried over Linde Molecular Sieves, no. 3A, and degassed before use. *trans*-$PF_2C_6H_{10}PF_2$[10] and $Mo(C_6H_5CH_3)_2$[11] were prepared according to the literature. $Mn(CO)_5Br$ was purchased from Strem Chemicals, Inc., Danvers, Mass., and was purified by high-vacuum sublimation immediately before use. $Fe(CO)_5$ was purchased from Ventron Corp., Beverly, Mass., and was filtered and vacuum distilled before use.

Preparation of Tris[1,2-bis(difluorophosphino)cyclohexane]molybdenum(0), $(PF_2C_6H_{10}PF_2)_3Mo$. A 0.688-g (3.13-mmol) sample of $PF_2C_6H_{10}PF_2$ was condensed onto 0.261 g (0.932 mmol) of $Mo(C_6H_5CH_3)_2$ at −196 °C. Upon warming to room temperature, the mixture turned red-brown indicating the occurrence of a reaction. The mixture was heated to 140 °C for several hours to ensure reaction completion. No change was observed in the mixture during heating. The solid was extracted with hexane and filtered on a medium-porosity glass frit. The filtrate was applied to a Florisil column. A light yellow band was eluted from the column with hexane. Light yellow crystals were obtained after solvent removal [mp 76–80 °C (uncor); 22% yield]. Anal. Calcd for $MoP_6F_{12}C_{18}H_{30}$: C, 28.57; H, 3.97; P, 24.60; mol wt 756. Found: C, 30.36; H, 4.18; P, 24.07; mol wt 772.

Preparation of *fac*-[1,2-Bis(difluorophosphino)cyclohexane]tricarbonylmanganese(I) Bromide, $(PF_2C_6H_{10}PF_2)Mn(CO)_3Br$, and Bis[1,2-bis(difluorophosphino)cyclohexane]carbonylmanganese(I) Bromide, $(PF_2C_6H_{10}PF_2)_2Mn(CO)Br$. An equimolar amount (approximately 1 mmol) of $PF_2C_6H_{10}PF_2$ was condensed onto a suspension of $Mn(CO)_5Br$ in ca. 35 mL of dry, air-free hexane in a 50-mL Pyrex vessel. The mixture was allowed to warm to room temperature and was irradiated with magnetic stirring for 20 h. At periodic intervals, the CO liberated during the reaction was removed while the reaction mixture was held at −196 °C. We recovered 1.8 equiv of CO/equiv of $Mn(CO)_5Br$. The solvent was removed under reduced pressure, and the resultant yellow-white solid was charged into a sublimation apparatus. A small amount of unreacted $Mn(CO)_5Br$ was recovered by careful sublimation below 60 °C. Yellow-orange crystals were obtained which sublimed at 70 °C [mp 96–98 °C (uncor); 21% yield] and were identified as the tricarbonyl. Anal. Calcd for $MnP_2F_4C_9H_{10}O_3Br$: C, 24.60; H, 2.28; P, 14.12; mol wt 439. Found: C, 24.80; H, 2.48; P, 13.96; mol wt 436. Light yellow crystals identified

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