Synthesis and reactivity of bidentate phosphine iron complex [(C2F5)2PCH2CH2P(C2F5)2]Fe(CO)3

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ionic crystals by piling the cluster anions and by surrounding the anion rows with cations. To put it in a rather crude way, we can look at these crystals as cocrystals whose structure is governed mainly by the steric similarity between the anions on one side and between the cations on the other (i.e. the similar packs better with the similar). In the case of carbonyl anions this preference can be assigned to the more effective interlocking possible between molecules with surface CO ligands. This situation recalls that observed in crystalline carbonyl–arene neutral clusters,[11b] where the crystal building process has to cope with the simultaneous presence of CO ligands and of flat arene fragments. In such cases the most efficient arrangement is invariably attained by grouping together in the lattice the fragments having similar shape, i.e. arenes with arenes and CO's with CO's.

Our analysis is necessarily very much qualitative. However, we would like to stress that a careful investigation of the molecular or ion organization in the crystal is the basis on which solid-state studies must be founded. For instance, it is worth recalling that several conducting materials have strongly anisotropic physical properties. This anisotropy usually arises from the molecular arrangement in the lattice. In organic conductors and superconductors, low-dimensionality (i.e. stacks of planar molecules or molecular piles and strings) is a prerequisite

for molecules or ions to carry electrons through the network.[28] Furthermore, several high-nuclearity clusters have been shown to possess physical properties distinct from both molecules and bulk metals (the "metametallic" state).[6,7]

We believe that, to be successful, the appreciation of the physical–chemical properties of these organometallic materials must rely not only on the knowledge of the structure of the component molecules or ions but also on information on the structure of the *entire* crystalline edifice.

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Synthesis and Reactivity of [(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$]Fe(CO)$_3$

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Reaction of (C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$ (1) with (benzylideneacetone)Fe(CO)$_3$ gives [(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P-(C$_2$F$_5$)$_2$]Fe(CO)$_3$ ((dfepe)Fe(CO)$_3$ (2)) in 59% yield. Photosubstitution of CO by L yields (dfepe)Fe(CO)$_2$L (L = THF, P(OCH$_3$)$_3$, C$_2$H$_4$). The ethylene complex has been characterized by single-crystal X-ray analysis (C$_{14}$H$_8$F$_{20}$FeO$_2$P$_2$, monoclinic, $P2_1/c$, a = 10.806 (5) Å, b = 14.069 (5) Å, c = 15.415 (3) Å, β = 101.61 (2)°, V = 2295.4 (14) Å^3, and Z = 4) and shows an unusually short carbon–carbon double bond (1.362 (7) Å) indicating weak π-back-bonding. Photolysis of 2 under 1 atm of acetylene yields the cyclopentadienone complex (η^4-C$_5$H$_4$O)Fe(CO)(dfepe) while irradiation in the presence of butadiene yields (η^4-C$_4$H$_6$)Fe-(CO)(dfepe). Three styrene complexes (η^6-C$_8$H$_8$)Fe(CO)(dfepe), (η^2-C$_8$H$_8$)Fe(CO)$_2$(dfepe), and (η^4-C$_8$H$_8$)Fe(CO)(dfepe) were isolated when 2 was photolyzed in the presence of styrene. The structure of the η^4-styrene complex was verified by a single-crystal X-ray analysis (C$_{19}$H$_{12}$F$_{20}$FeOP$_2$, triclinic, $P\bar{1}$, a = 8.7382 (16) Å, b = 10.789 (3) Å, c = 15.652 (6) Å, α = 87.382 (16)°, β = 101.61 (2)°, γ = 73.857 (17)°, V = 1262.9 (6) Å^3, and Z = 2). The η^4-styrene complex can be used as an efficient (dfepe)Fe(CO)-transfer agent. Photolysis of 2 under 1 atm of H$_2$ gave the fluxional *cis*-dihydride complex (dfepe)(CO)$_2$Fe(H)$_2$ (17). Attempted oxidative addition of Et$_3$SiH to photogenerated (dfepe)Fe(CO)$_2$ gave dihydride complex 17 and (Et$_3$Si)$_2$O. Photolysis of 2 in alkane solvents at temperatures from –50 to +25 °C gave no evidence for oxidative addition adducts.

Introduction

There are a limited number of bidentate ligands with strong π-accepting properties available for use in synthesis and stabilization of low-valent transition-metal complexes.[1–7] An attractive class of such ligands is the per-

fluorinated bidentate alkyl phosphines, (R$_f$)$_2$PCF$_2$CF$_2$P-(R$_f$)$_2$ (R$_f$ = perfluoroalkyl). It is well-established that (CF$_3$)$_3$P is similar to CO in its π-acceptor properties, and thus (R$_f$)$_2$PCF$_2$CF$_2$P(R$_f$)$_2$ complexes represent chelates which should mimic the electronic properties of two cis carbonyl ligands. Aside from the usual advantages of chelates, several other features of these ligands are of interest: (1) The steric bulk of the ligands can be varied by changing R$_f$. (2) The presence of highly lipophilic R$_f$

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Table I. ν(CO) Stretching Frequencies for Iron Carbonyl Complexes of the Type $L_2Fe(CO)_3$

compd	phase	freq, cm^{-1}			ref
$(Ph_2PCH_2CH_2PPH_2)Fe(CO)_3$	CH_2Cl_2	1992 (s)	1923 (m)	1901 (s)	a
$[(CH_3)_2PCF_2C_2P(CH_3)_2]Fe(CO)_3$	CH_2Cl_2	1994 (s)	1925 (m)	1910 (vs)	b
$(F_3P)_2Fe(CO)_2$ C_{2v}	gas	2079 (m)		2026 (vs)	c
$(F_3P)_2Fe(CO)_3$ C_s	gas	2084 (m)		2001 (s)	c
$(F_3P)_2Fe(CO)_3$ D_{3h}	gas	2005 (s)			c
$[(CF_3)_3P]_2Fe(CO)_3$ C_{2v}	gas	2080 (m)		2025 (s)	d
$(dfepe)Fe(CO)_3$	pentane	2055 (s)	2004 (m)	1991 (s)	this work

a Manuel, T. A. *Inorg. Chem.* **1963**, *2*, 854. *b* Langford, B. R.; Akhtar, M.; Ellis, P. D.; MacDiarmid, A. G.; Odom, J. D. *Inorg. Chem.* **1975**, *14*, 2937. *c* Tripathi, J. B. PD.; Bigorgne, M. *J. Organomet Chem.* **1967**, *9*, 307. *d* Burg, A. B. *Inorg. Chem.* **1986**, *25*, 4751.

groups should enhance the solubility of complexes in inert, nonpolar solvents (including fluorocarbons). (3) No C–H bonds or other reactive functional groups are present which could deactivate reactive unsaturated intermediates by coordination or oxidative addition. (4) The P–R$_f$ bond is substantially more inert than the P–F bond, and thus such species offer advantages over complexes of the type $F_2PCX_2CX_2PF_2$.[2]

Burg, in the early 1960s, prepared $(CF_3)_2PCX_2CX_2P$-$(CF_3)_2$ (X = H, F), the first examples of this class of ligand, together with the nickel carbonyl complexes $(CF_3)_2PCX_2CX_2P(CF_3)_2Ni(CO)_2$ (X = H, F).[3] The difficult and specialized procedures involved in preparing these ligands limited their further development. Recently, however, more general routes to these ligands have become available. Cavell[4] has prepared $(CF_3)_2P(CH_2)_nP(CF_3)_2$ (n = 1–3), $(CF_3)_2PCH(CH_3)P(CF_3)_2$, $(CF_3)_2PC(CH_3)_2P(CF_3)_2$, and $(CF_3)_2PCF_2CF_2P(CF_3)_2$ by reaction of $(CF_3)_2P–P(CF_3)_2$ with the appropriate alkyl or perfluoroalkyl diiodides. Pt(II) derivatives of several of these ligands were prepared along with molybdenum derivatives $(CO)_4Mo$-$[(CF_3)_2PCX_2CX_2P(CF_3)_2]$ (X = H, F) and $(CO)_4Mo[(CF_3)_2P(CH_2)_3P(CF_3)_2]$. Roddick[5] has reported a convenient synthesis of $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ (termed dfepe) via conversion of C_2F_5Cl to C_2F_5Li with *n*-BuLi at –100 °C followed by reaction with $Cl_2PCH_2CH_2PCl_2$. This ligand has been used to prepare $(dfepe)Cr(CO)_4$ and $(dfepe)Mo$-$(CO)_4$[5] as well as $(\eta^6$-$C_6H_5CH_3)Mo(dfepe)(L)$[6] where L = CO, H_2, CH_3CN, N_2, and THF and $Ru(dfepe)_2(H)_2$.[7] Analysis of the CO-stretching frequencies of the nickel, molybdenum, and chromium carbonyl derivatives cited above show clearly that these bidentate ligands are strong π-acceptors.

In this paper we report our investigations of the synthesis, structure, and reactivity of $(C_2F_5)_2PCH_2CH_2P(C_2$-$F_5)_2$ (1) derivatives of iron(0) complexes.

Results and Discussion

Synthesis and Characterization of (dfepe)Fe(CO)$_3$ (2). Complex 2 was prepared by displacement of benzylideneacetone (BDA) from $(BDA)Fe(CO)_3$ by 1 in toluene at 110 °C. The tricarbonyl 2 is a yellow oil at 25 °C which is highly soluble in hydrocarbon and perfluorocarbon solvents. The infrared spectrum in pentane shows three strong ν_{CO} bands at 2055, 2004, and 1991 cm^{-1}. Roddick[7] has recently reported the synthesis of the ruthenium analogue, $Ru(dfepe)(CO)_3$, by reaction of $Ru(dfepe)_2(H)_2$ with CO (ν_{CO} bands at 2068, 2019, 1996 cm^{-1}). The infrared data for 2 are compared to ν_{CO} data for other complexes of the type $L_2Fe(CO)_3$ in Table I. Qualitative comparison of these data shows, as noted earlier for such ligands, that dfepe is a strong π-acceptor bidentate ligand comparable to two cis PF$_3$ or two cis CO ligands. For example, the stretching frequencies of 2 are substantially higher than the diphos analogue $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Fe(CO)_3$ and comparable to $(F_3P)_2Fe(CO)_3$ derivatives. While several structures are possible for 2 we favor a trigonal-

bipyramidal geometry in which the bidentate phosphine spans the axial–equatorial sites. In a five-membered ring,

2
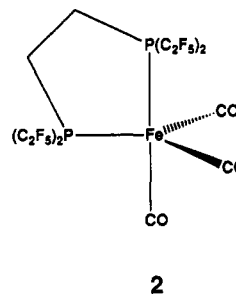
axial–equatorial substitution minimizes the ring strain,[8] as found in X-ray structures of $[(C_6H_5)_2PCH_2CH_2P(C_6$-$H_5)_2]Fe(CO)_3$[9] and $[(C_6H_{11})_2PC{=}C[P(C_6H_{11})_2]CF_2CF_2]$-$Fe(CO)_3$.[10] The ethylene derivative $(dfepe)Fe(CO)_2(C_2H_4)$ adopts such a geometry in which an equatorial CO has been replaced by C_2H_4 (see below). The infrared data are consistent with this structure. The NMR data indicate a rapidly fluxional molecule typical of five-coordinate systems of the type $Fe(CO)_3L_2$. The ^{13}C spectrum shows a single carbonyl resonances at 211 ppm (broadened due to ^{31}P coupling), and the ^{31}P spectrum exhibits a single band at 140 ppm (quintet, $^2J_{PF}$ = 66 Hz). In the ^{19}F spectrum the CF$_3$ groups appear as a singlet at δ –13.3 ppm while the diastereotopic fluorines of the CF$_2$ groups appear as an AB pattern centered at –46.2 ppm ($^2J_{FF}$ = 314 Hz, $^2J_{PF_a}$ = 65 Hz, $^2J_{PF_b}$ = 61 Hz). The exchange process likely occurs via a Berry pseudorotation mechanism as proposed for complexes of similar structures. The ^{13}C and ^{31}P spectra show no line broadening down to –80 °C, which indicates a barrier to isomerization of less than ca. 7–8 kcal/mol.

Photochemistry of [Bis[bis(pentafluoroethyl)-phosphino]ethane]tricarbonyliron, Fe(dfepe)(CO)$_3$ (2). In order to access a variety of derivatives of $(dfepe)Fe^0$, methods were sought to replace the carbonyl ligands of 2. Thermal substitution of CO in $Fe(CO)_5$ requires high temperatures,[11] and we were concerned about the thermal lability of dfepe in 2 under such conditions (see below). Thus, initial efforts were directed at photochemical substitutions with the goal of directly introducing various ligands or replacing CO with a labile molecule

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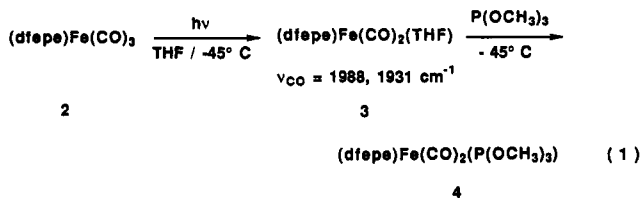
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which could subsequently be readily replaced.

Photolysis of 2 in THF. Photolysis of 2 in THF solution, at −45 °C, leads to formation of a new species with ν_{CO} at 1988 and 1931 cm^{-1} (eq 1). This species is assigned

(dfepe)Fe(CO)₃ $\xrightarrow[\text{THF / -45° C}]{h\nu}$ (dfepe)Fe(CO)₂(THF) $\xrightarrow[\text{- 45° C}]{P(OCH_3)_3}$

ν_{CO} = 1988, 1931 cm^{-1}

2   **3**

(dfepe)Fe(CO)₂(P(OCH₃)₃)   (1)

4

to the THF adduct Fe(dfepe)(CO)₂(THF) (3). A similar THF adduct was reported during the photolysis of (C₄H₄)Fe(CO)₃ in THF.[12] Complex 3 is too unstable to isolate (decomposition in solution occurs over 5 h at −30 °C); however, evidence for the presence of 3 comes from reaction with P(OCH₃)₃. Addition of P(OCH₃)₃ to a THF solution of 3 at −45 °C in the dark affords exclusively Fe(dfepe)(CO)₂[P(OCH₃)₃] (4), which has been isolated and characterized (see below). (P(OCH₃)₃ does not react in the dark with 2 in THF.) The ready generation and high reactivity of 3 makes it a convenient thermal source of "(dfepe)Fe(CO)₂".

Photosubstitution by P(OCH₃)₃. Photolysis of 2 in diethyl ether at −45 °C in the presence of P(OCH₃)₃ gives the phosphite adduct 4 (yellow crystals, 80% yield), which exhibits two ν_{CO} bands at 1988 and 1973 cm^{-1}. In the ^{13}C NMR spectrum, the carbonyl carbons show a single resonance at δ 212 ppm (d, $^2J_{PC}$ = 50 Hz), while the ^{31}P spectrum exhibits a triplet at δ 173 ppm for P(OMe)₃ ($^2J_{PP}$ = 8 Hz) and a broad quintet at δ 133 ppm ($^2J_{FP}$ = 59 Hz) for both bidentate ^{31}P nuclei. The structure most consistent with the IR and NMR data is one in which phosphite ligand occupies an equatorial site and the bidentate ligand spans the normally preferred axial–equatorial positions. This small $^2J_{PP}$ is indicative of a cis relationship


4
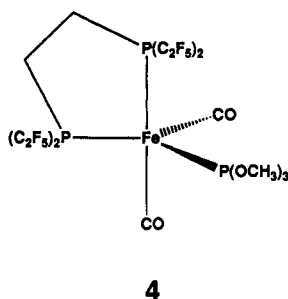
between the phosphite phosphorus atom and both bidentate phosphorus atoms and supports the assignment of structure 4.[13] Analysis of the relative CO intensities gives a calculated OC–Fe–CO angle of ca. 99°.[14] The observation of a single ^{13}CO resonances and a single ^{31}P resonance for the bidentate ligand reflects the expected highly fluxional character of 4.

Photosubstitution by C₂H₄. Photolysis of 2 in a diethyl ether solution saturated with ethylene gives the ethylene complex (dfepe)Fe(CO)₂(C₂H₄) (5), which can be isolated as a crystalline solid in good yields (70%). The infrared spectrum shows two strong ν(CO) bands at 2020 and 1979 cm^{-1} consistent with cis carbonyl groups. Key

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Table II. Crystallographic Data and Collection Parameters and Refinement Parameters for (CO)₂(dfepe)Fe(η²-CH₂=CH₂) (5) and (CO)(dfepe)Fe(η⁴-C₆H₅CH=CH₂) (13)

	5	13
molecular formula	C₁₄H₈F₂₀FeO₂P₂	C₁₉H₁₂F₂₀FeOP₂
fw	705.97	754.06
cryst dimens, mm	0.25 × 0.30 × 0.50	0.30 × 0.30 × 0.20
space group	*P2₁/c*	*P1̄*
cell params		
a, Å	10.806 (5)	8.7382 (16)
b, Å	14.069 (5)	10.789 (3)
c, Å	15.415 (3)	15.652 (6)
α, deg		87.382 (16)
β, deg	101.6 (2)	69.432 (24)
γ, deg		73.857 (17)
V, Å³	2295.4 (14)	1262.9 (6)
Z	4	2
d(calcd), Mg/m³	2.043	1.983
F(000)	1136	739.92
radiation (wavelength, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
monochromator	graphite	graphite
linear abs coeff, mm⁻¹	0.94	0.88
scan mode	ω–2θ	ω–2θ
background	25% of full scan width on both sides	25% of full scan width on both sides
2θ limits, deg	2 < 2θ < 45	2 < 2θ < 50
octants colled	±h,k,l	±h,k,±l
total no. unique reflns	2975	4409
data with *I* ≥ 2.5σ(*I*)	2209	3630
R (including unobserveds)	0.035 (0.053)	0.044 (0.054)
*R*_w (including unobserveds)	0.033 (0.033)	0.049 (0.049)
GoF	1.84	2.82
no. of params	385	437
largest param shift/error	0.28	0.308
max density in final difference synthesis, e/Å³	0.320	0.680

NMR spectral parameters of the C₂H₄ ligand and ^{1}H δ 2.4 ppm (t, $^3J_{PH}$ = 3 Hz); ^{13}C δ 39.9 ppm (J_{CH} = 160 Hz). The data are similar to those for the parent complex[15] (CO)₄Fe(η²-C₂H₄): ^{1}H δ 2.45 ppm; ^{13}C δ 35.3 ppm. No decoalescence of the ^{1}H signal of the C₂H₄ ligand occurred down to −60 °C in CD₂Cl₂. Below −60 °C the complex precipitated from the solution. While the parent complex (CO)₄Fe(C₂H₄) is an oil unstable above −10 °C, the dfepe derivative 5 is quite stable at 25 °C for extended periods of time.

5
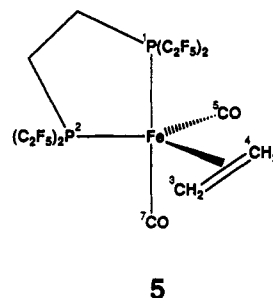
X-ray Structure Determination of 5. The structure of 5 was confirmed by a single-crystal X-ray structure determination. Single crystals for X-ray analysis were grown from a saturated solution of hexane at −30 °C. Complex 5 crystallizes in the monoclinic system with space group *P2₁/c*. The unit cell contains four molecules separated by the normal van der Waals distances. Crystallographic data are collected in Table II, and atomic coordinates are listed in Table III. An ORTEP diagram of 5

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Table III. Fractional Atomic Coordinates and Isotropic Thermal Parameters for (CO)₂(dfepe)Fe(η²-CH₂=CH₂) (5)

| atom	x	y	z	B_{iso}, Å²^a
Fe(1)	0.70629 (6)	0.89945 (4)	0.17854 (4)	3.24 (3)
P(1)	0.54942 (10)	0.84621 (7)	0.23735 (7)	3.10 (5)
P(2)	0.81324 (10)	0.78986 (8)	0.25586 (7)	3.42 (5)
C(1)	0.5849 (4)	0.7254 (3)	0.2807 (3)	3.66 (20)
C(2)	0.7238 (4)	0.7181 (3)	0.3212 (3)	4.02 (21)
C(3)	0.7417 (4)	1.0270 (3)	0.2532 (3)	4.71 (23)
C(4)	0.6847 (4)	1.0444 (3)	0.1778 (3)	5.1 (3)
C(5)	0.6296 (4)	0.8670 (3)	0.0700 (3)	4.50 (22)
O(6)	0.5891 (3)	0.84889 (24)	-0.00290 (19)	6.66 (19)
C(7)	0.8385 (4)	0.9323 (3)	0.1332 (3)	4.70 (24)
O(8)	0.9219 (3)	0.9551 (3)	0.10288 (23)	7.43 (21)
C(11)	0.3384 (4)	0.8205 (3)	0.1655 (3)	4.08 (21)
C(12)	0.3100 (5)	0.9024 (4)	0.1178 (3)	5.8 (3)
F(13)	0.31410 (22)	0.77461 (18)	0.21238 (17)	5.48 (13)
F(14)	0.40927 (25)	0.75959 (18)	0.10210 (16)	5.79 (13)
F(15)	0.3664 (3)	0.93989 (25)	0.05779 (21)	9.47 (20)
F(16)	0.1995 (3)	0.87678 (25)	0.07865 (25)	10.28 (22)
F(17)	0.3001 (3)	0.97142 (21)	0.17208 (20)	9.12 (20)
C(21)	0.5089 (4)	0.9094 (3)	0.3394 (3)	3.71 (21)
C(22)	0.4011 (4)	0.8804 (3)	0.3853 (3)	4.82 (25)
F(23)	0.49300 (24)	1.00281 (15)	0.32178 (16)	5.03 (13)
F(24)	0.61600 (22)	0.89863 (18)	0.40158 (14)	4.99 (13)
F(25)	0.29103 (23)	0.90353 (20)	0.33753 (19)	6.49 (16)
F(26)	0.4141 (3)	0.92602 (21)	0.46210 (18)	7.51 (17)
F(27)	0.4010 (3)	0.78798 (18)	0.40136 (17)	6.28 (15)
C(31)	0.8974 (5)	0.6947 (3)	0.2002 (3)	5.5 (3)
C(32)	0.8254 (6)	0.6525 (4)	0.1170 (3)	7.0 (3)
F(33)	0.9362 (3)	0.62229 (19)	0.25679 (18)	6.78 (15)
F(34)	1.0054 (3)	0.73566 (21)	0.17708 (20)	7.35 (18)
F(35)	0.8889 (4)	0.57970 (21)	0.09237 (21)	10.10 (23)
F(36)	0.8103 (3)	0.71482 (21)	0.05109 (17)	8.11 (19)
F(37)	0.7150 (3)	0.62479 (22)	0.13282 (22)	8.37 (19)
C(41)	0.9528 (4)	0.8316 (3)	0.3440 (3)	4.8 (24)
C(42)	10.439 (5)	0.7658 (4)	0.4051 (3)	6.7 (3)
F(43)	1.02401 (23)	0.89057 (20)	0.30436 (17)	6.35 (15)
F(44)	0.89968 (24)	0.88582 (19)	0.39898 (15)	5.78 (14)
F(45)	1.1220 (3)	0.72225 (23)	0.36109 (21)	8.36 (18)
F(46)	1.1137 (3)	0.8144 (3)	0.46928 (20)	9.25 (19)
F(47)	0.9807 (3)	0.69946 (22)	0.43860 (19)	7.67 (17)

^{a} B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Table IV. Selected Bond Distances (Å) and Angles (deg) for (dfepe)(CO)₂Fe(η²-CH₂=CH²) (5)

C(3)–C(4)	1.362 (7)	C(5)–Fe	1.771 (4)
C(3)–Fe	2.125 (4)	C(7)–Fe	1.773 (5)
P(1)–Fe	2.2078 (15)	C(4)–Fe	2.113 (4)
P(2)–Fe	2.1398 (13)		
P(2)–Fe–P(1)	84.27 (5)	P(1)–Fe–C(3)	97.68 (12)
Fe–C(3)–C(4)	70.8 (3)	P(1)–Fe–C(4)	96.10 (13)
Fe–C(4)–C(3)	71.7 (3)	C(1)–Fe–C(3)	85.53 (19)
P(1)–Fe–C(5)	92.76 (14)	C(1)–Fe–C(4)	88.81 (19)
P(1)–Fe–C(7)	184.97 (14)	C(2)–Fe–C(4)	99.81 (19)
C(7)–Fe–C(5)	87.47 (20)	P(2)–Fe–C(3)	106.79 (13)
P(2)–Fe–C(5)	115.99 (14)	C(3)–Fe–C(4)	37.49 (18)
P(2)–Fe–C(7)	91.11 (14)		

is shown in Figure 1, and selected bond distances and angles are summarized in Table IV. The configuration around the central iron atom approximates a trigonal bipyramid. One carbonyl group, the ethylene ligand and P(2) of the bidentate ligand occupy the three equatorial positions; P(1) and the remaining carbonyl group occupy the two axial sites [P(1)–Fe–C(7) = 175°]. The P(1)–Fe–P(2) angle of 84° is similar to values found in other ethano-bridged bidentate phosphine complexes.[6,7,9,10] The angles between the midpoint of C(3) and C(4) of the ethylene ligand, iron, and P(2) and C(5), respectively are 126 and 119°. Similarly, P(1)–Fe–midpoint (C(4)C(3)) and C(7)–Fe–midpoint (C(4)C(3)) are 98 and 87°.

For maximum back-bonding, the ethylene carbons should lie in the equatorial plane. This geometry is observed in 5. If the equatorial plane is defined as the plane
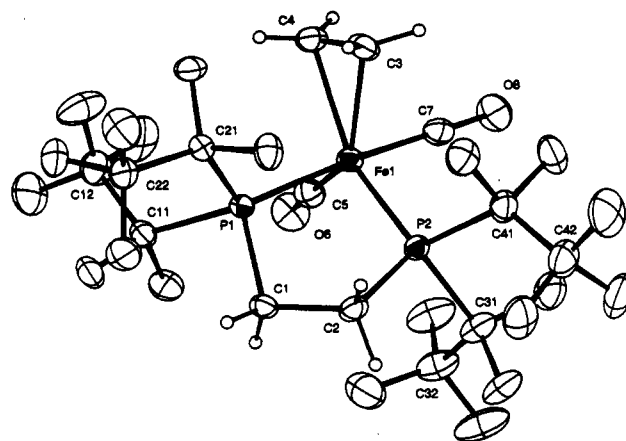

Figure 1. ORTEP diagram of (dfepe)(CO)₂Fe(η²-CH₂=CH₂).

containing P(2), Fe, and C(5), then the Fe–C(4)–C(3) plane subtends an angle of only 8° with this plane. C(3) and C(4) lie 0.23 and 0.06 Å above the plane, respectively. The axial Fe–P(1) distance [2.2078 (15) Å] is in agreement with the Fe–P$_{ax}$ distances found in the literature.[9,10] The equatorial Fe–P(2) [2.1398 (13) Å] distance is similar to that of [(CF₃)₃P]₃Fe(CO)₂ [2.151 (4) Å][16] but shorter than the Fe–P$_{eq}$ distance in (dppe)Fe(CO)₃ [2.227 (2) Å],[9] as expected with a better π-acid ligand. The bond distances observed for 5 are consistent with those found for similar complexes. Table V compares key distances for 5, (CO)₄Fe(C₂H₄), and (CO)₃[P(C₆H₅)₃]Fe(C₂H₄). The most notable structural feature of 5 is the remarkably short carbon–carbon length of 1.362 (7) Å for the coordinated ethylene ligand. This distance is one of the shortest known for a coordinated ethylene and is comparable to that in Zeise's salt [KPt(C₂H₄))Cl₃]·H₂O [1.354 (15) Å].[17] This short length in 5 reflects poor back-bonding to the π* orbitals of ethylene and is a consequence of the strong π-acid character of the fluorinated bidentate phosphine ligand.[18] The C–C bond length in (Ph₃P)(CO)₃Fe(C₂H₄)[15] is somewhat longer (1.398 (8) Å), no doubt due to increased back-bonding as a consequence of the better donor, poorer acceptor properties of P(C₆H₅)₃ relative to the (perfluoroalkyl)phosphine. A comparison with the C–C bond length of (CO)₄Fe(C₂H₄) determined by electron diffraction is not meaningful due to the high degree of uncertainty in this length [1.46 (6) Å].[19]

Synthesis of other η²-olefin complexes using similar experimental conditions has been attempted. The propene complex (dfepe)Fe(CO)₂(η²-C₃H₆) (6) could be isolated as a yellow oil which was too thermally unstable at 25 °C to provide an analytically pure sample. Likewise, photolysis of 2 in cyclohexene at –45 °C led to IR evidence for formation of (dfepe)Fe(CO)₂(η²-C₆H₁₀) (7) (ν_{CO} = 2004, 1966 cm⁻¹), but isolation of a complex stable at 25 °C was not possible.

Photoreaction of 2 with Acetylene. Photolysis of 2 in an ether solution saturated with acetylene led not to the formation of an η²-adduct but rather to the η⁴-cyclopentadienone complex 8, (dfepe)Fe(CO)(η⁴-C₄H₄CO) (30% yield, yellow crystals). The ¹³C NMR shift for the vinylic ring carbons [δ 67 and 81 ppm] indicate that the two double bonds are η²-coordinated while the keto group [ν_{CO}

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8
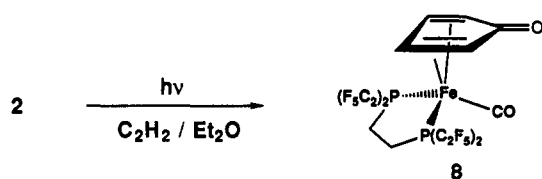
$= 1646$ cm^{-1} and $\delta_{CO} = 172.5$ ppm] is not bound to iron. This reaction is well-known for simple iron carbonyl derivatives,[20] but yields of dienone products are generally quite low.

Photosubstitution of Butadiene. Generally, Fe(η^4-diene)L$_3$ [L = PF$_3$, P(OCH$_3$)$_3$] complexes have been prepared by photolysis of FeL$_5$,[21] by reduction of FeCl$_2$ in presence in dienes and L,[22] or by metal atom evaporation techniques.[23] Complexes of the type (η^4-diene)Fe(CO)L$_2$ [L = PF$_3$,[24] P(OCH$_3$)$_3$,[25] L$_2$ = dppe[26]] have been described. These systems have been prepared from (η^4-C$_4$H$_6$)$_2$Fe(CO) by thermal or photochemical displacement of butadiene but not from carbonyl substitution starting from L$_2$Fe(CO)$_3$ derivatives. In view of the ready substitution of CO in **2** by monodentate ligands, we sought to prepare bidentate derivatives by similar techniques.

Photolysis of **2** was carried out in an ether solution of butadiene at 0 °C and monitored by IR spectroscopy. The bands for **2** disappear as a strong single band grows at 1996 cm^{-1}, supporting the formation of the η^4-diene monocarbonyl complex (dfepe)Fe(CO)(η^4-C$_4$H$_6$) (**9**). Complex

9
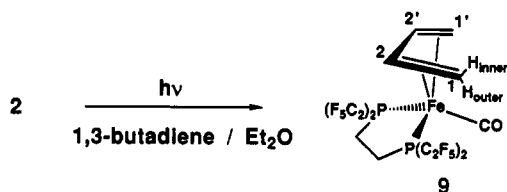
9 was isolated as an analytically pure yellow crystalline material (40%). The ^{1}H and ^{13}C NMR data clearly support η^4-coordination of the diene ligand ($\delta_{H(1)(inner)} = 0.05$ ppm, $\delta_{H(1)(outer)} = 2.1$ ppm $\delta_{C(2)} = 84.8$ ppm $\delta_{C(1)} = 38.7$ ppm). The similarities of the ν_{CO} bands of **9** and (η^4-C$_4$H$_6$)Fe(CO(PF$_3$)$_2$,[24] 1996 and 2001 cm^{-1}, respectively, again support the suggestion that the dfepe ligand has π-acidic character nearly equivalent to two PF$_3$ ligands. No reaction of **9** is observed under carbon monoxide (1 atm in THF) or in the presence of trimethyl phosphite either under photolytic or thermal conditions.

Photoreactions with Methyl Vinyl Ketone and Styrene: Synthesis of (dfepe)Fe(CO)-Transfer Reagents. α,β-Unsaturated ketone complexes of Fe(CO)$_3$ have been successfully used as Fe(CO)$_3$-transfer reagents under very mild conditions.[27] The utility of such reagents

led us to investigate the synthesis of (dfepe)(CO)Fe(enone) complexes which could serve as convenient transfer reagents for the (dfepe)(CO)Fe moiety.

Photolysis of **2** at 0 °C in methyl vinyl ketone led to formation of a blood red solution in which the ν_{CO} bands for **2** had been replaced by two new bands at 2020 and 1976 cm^{-1}. From this solution the (dfepe)(CO)Fe(η^4-methyl vinyl ketone) complex **10** ($\nu_{CO} = 1976$ cm^{-1}) could be iso-

10
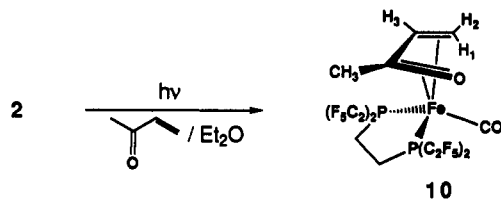
lated in 20% yield as a dark red analytically pure crystalline material. Owing to the low yield of this material and the extreme sensitivity of **10**, it was not practical to develop the transfer chemistry of this complex.

While styrene is often a quite labile ligand, styrene complexes have seldom been employed synthetically as transfer reagents. One exception is the use of Fe(CO)$_4$-(styrene) to prepare other alkene complexes.[28] On the basis of the stability of iron carbonyl complexes **11** and **12**,[29] we anticipated that an η^4-styrene complex of (dfepe)Fe(CO) may be accessible and serve as a convenient thermal source of "(dfepe)Fe(CO)".

11   **12**
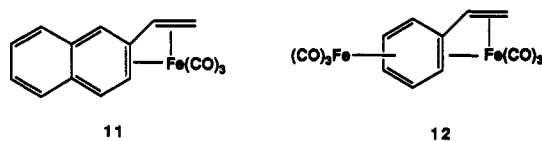
When **2** is photolyzed in the presence of styrenes, three complexes **13–15** corresponding to η^4-, η^2-, and η^6-styrene coordination could be isolated in 55%, 20%, and 5%

13   **14**   **15**
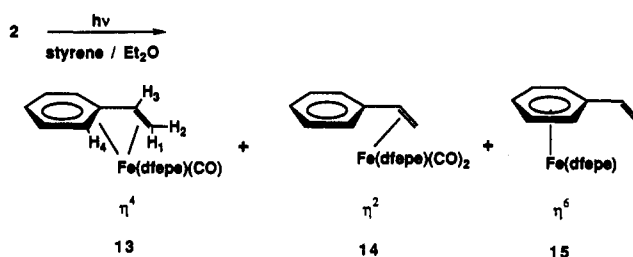
yields, respectively. Following the progress of the reaction of IR spectroscopy suggested that the η^2-complex **14** is a precursor to the η^4-complex **13**. However, photolysis of a pure sample of the η^4-complex **13** did not lead to the formation of the η^6-complex **15**.

The minor products η^2-**14** and η^6-**15** were characterized by IR and NMR spectroscopy; complete details are given in the Experimental Section. The structure of the η^2-dicarbonyl complex **14** was confirmed by the presence of two ν_{CO} bands at 2021 and 1982 cm^{-1} similar to the ethylene complex **5**($\nu_{CO} = 2020$ and 1979 cm^{-1}) and the observation of ^{13}C resonances at δ 32.1 and 57.1 ppm attributable to C$_\beta$ and C$_\alpha$ of the coordinated vinyl group. These resonances are each shifted upfield ca. 80 ppm relative to the shifts in free styrene (δ 112 and 136 ppm, respectively) and are in accord with the 92 ppm upfield shift of the olefin

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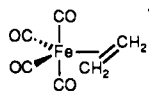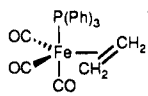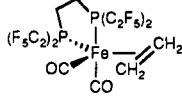
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Brookhart et al.

Table V. Relevant Bond Lengths (Å) of Fe(0) η^2-Ethylene Complexes

	a	b	(this work)
Fe–P$_{ax}$		2.265 (1)	2.2078 (15)
Fe–P$_{e}$q			2.1398 (13)
Fe–CO$_{ax}$	1.796 (35)	1.759 (3)	1.771 (4)
Fe–CO$_{eq}$	1.836 (35)	1.759 (6), 1.763 (6)	1.773 (5)
Fe–C$_{ethylene}$	2.117 (3)	2.095 (7), 2.102 (7)	2.125 (4), 2.113 (4)
ethylene C–C	1.46 (6)	1.398 (8)	1.362 (7)

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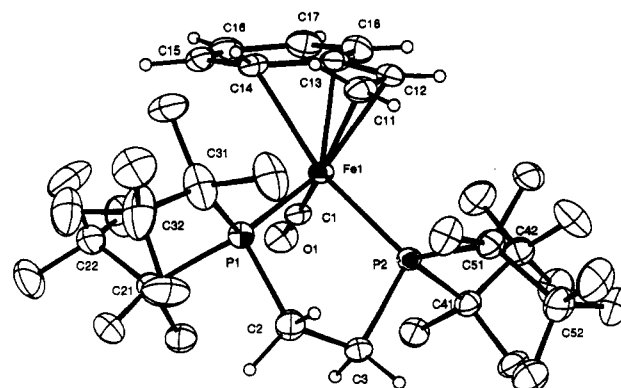
Table VI. Fractional Atomic Coordinates and Isotropic Thermal Parameters for (CO)(dfepe)Fe(η^4-C₆H₅CH=CH₂) (13)

atom	x	y	z	B_{iso}, Å^{2} ^{a}
Fe(1)	0.53799 (6)	0.79746 (5)	0.29625 (3)	3.025 (22)
P(1)	0.72546 (12)	0.76618 (10)	0.17117 (7)	3.59 (5)
P(2)	0.58658 (11)	0.99889 (9)	0.24936 (6)	3.16 (4)
C(1)	0.3635 (4)	0.8572 (3)	0.25003 (24)	3.55 (18)
O(1)	0.2486 (3)	0.8897 (3)	0.22229 (21)	5.43 (17)
C(2)	0.8203 (5)	0.9208 (4)	0.0985 (3)	5.43 (24)
C(3)	0.6945 (5)	1.0464 (4)	0.1189 (3)	4.75 (22)
C(11)	0.6827 (5)	0.7057 (4)	0.3941 (3)	4.65 (21)
C(12)	0.5171 (5)	0.7439 (4)	0.43930 (24)	4.33 (21)
C(13)	0.3961 (5)	0.6842 (4)	0.43379 (23)	4.03 (19)
C(14)	0.4524 (5)	0.5932 (4)	0.3778 (3)	4.10 (20)
C(15)	0.3308 (5)	0.5449 (4)	0.3630 (3)	4.73 (21)
C(16)	0.1686 (6)	0.5838 (5)	0.4001 (3)	5.61 (25)
C(17)	0.1117 (5)	0.6705 (4)	0.4571 (3)	5.59 (24)
C(18)	0.2211 (5)	0.7197 (4)	0.4735 (3)	5.16 (24)
C(21)	0.6758 (5)	0.7464 (4)	0.0680 (3)	4.35 (22)
C(22)	0.5831 (6)	0.6345 (4)	0.0888 (3)	5.45 (25)
F(23)	0.5736 (3)	0.86467 (22)	0.03609 (16)	5.64 (14)
F(24)	0.8100 (3)	0.73715 (25)	−0.00671 (16)	5.67 (14)
F(25)	0.4284 (3)	0.6577 (3)	0.14151 (21)	7.91 (20)
F(26)	0.5747 (4)	0.6226 (3)	0.01037 (20)	9.02 (22)
F(27)	0.6540 (4)	0.5185 (3)	0.1381 (3)	9.51 (24)
C(31)	0.9199 (6)	0.6298 (6)	0.1864 (4)	7.6 (4)
C(32)	1.0497 (7)	0.5805 (6)	0.1188 (5)	10.0 (5)
F(33)	0.9923 (3)	0.6782 (3)	0.23082 (22)	8.19 (21)
F(34)	0.8670 (3)	0.55065 (24)	0.25494 (18)	6.75 (15)
F(35)	1.1734 (3)	0.5001 (3)	0.15394 (23)	8.25 (19)
F(36)	1.0998 (4)	0.7025 (3)	0.04786 (20)	9.16 (21)
F(37)	1.0021 (4)	0.5112 (3)	0.08163 (25)	9.29 (24)
C(41)	0.4138 (5)	1.1524 (3)	0.2476 (3)	3.88 (19)
C(42)	0.2890 (5)	1.1596 (4)	0.3423 (3)	4.90 (22)
F(43)	0.4727 (3)	1.27026 (20)	0.20522 (16)	5.21 (13)
F(44)	0.3267 (3)	1.15024 (22)	0.19176 (16)	5.29 (13)
F(45)	0.3639 (3)	1.1573 (3)	0.40278 (18)	7.58 (19)
F(46)	0.1774 (3)	1.2704 (3)	0.33250 (21)	7.71 (18)
F(47)	0.2086 (3)	1.0559 (3)	0.38284 (20)	7.12 (16)
C(51)	0.7336 (5)	1.0375 (4)	0.3000 (3)	4.47 (22)
C(52)	0.7823 (6)	1.1775 (5)	0.2723 (3)	5.8 (3)
F(53)	0.8793 (3)	0.95493 (24)	0.27361 (19)	5.95 (16)
F(54)	0.6791 (3)	0.99613 (23)	0.39707 (16)	5.47 (18)
F(55)	0.8313 (4)	1.2318 (3)	0.17850 (19)	7.57 (18)
F(56)	0.9083 (3)	1.1593 (3)	0.30717 (23)	8.16 (21)
F(57)	0.6594 (3)	1.26185 (24)	0.30969 (19)	6.61 (17)

^{a} B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Figure 2. ORTEP diagram of (dfepe)(CO)Fe(η^4-CH₆H₅CH=CH₂).

Table VII. Selected Bond Distances (Å) and Angles (deg) for (dfepe)(CO)Fe(η^4-C₆H₅CH=CH₂) (13)

Fe–P(1)	2.1364 (13)	C(14)–C(13)	1.431 (5)
Fe–P(2)	2.1313 (11)	C(11)–C(12)	1.389 (6)
Fe–C(11)	2.111 (4)	C(12)–C(13)	1.423 (5)
Fe–C(12)	2.045 (3)	C(14)–C(15)	1.423 (5)
Fe–C(13)	2.045 (3)	C(15)–C(16)	1.340 (6)
Fe–C(14)	2.278 (4)	C(160C(17)	1.405 (7)
Fe–C(1)	1.773 (4)	C(17)–C(18)	1.348 (6)
		C(18)–C(13)	1.434 (5)

P(1)–Fe–P(2)	88.30 (5)	C(1)–Fe–C(11)	160.73 (16)
P(2)–Fe–C(1)	90.60 (11)	P(1)–Fe–C(11)	97.90 (12)
P(1)–Fe–C(1)	99.28 (12)	P(1)–Fe–C(12)	136.67 (12)
Fe–C(13)–C(14)	75.73 (20)	P(2)–Fe–C(14)	167.02 (10)
C(1)–Fe–C(12)	136.67 (12)	Fe–C(14)–C(13)	66.76 (19)
Fe–C(11)–C(12)	67.95 (21)	P(2)–Fe–C(12)	100.52 (11)
P(2)–Fe–C(13)	129.52 (11)	Fe–C(12)–C(11)	73.03 (21)
C(13)–C(14)–C(15)	117.9 (3)	C(17)–C(18)–C(13)	120.8 (4)
P(2)–Fe–C(11)	98.58 (11)	C(14)–C(13)–C(18)	118.5 (3)
C(14)–C(15)–C(16)	121.1 (4)	C(16)–C(17)–C(18)	120.0 (4)
C(15)–C(16)–C(17)	121.6 (4)		

resonance in **5** (δ 36 ppm) relative to that in free ethylene (δ 128 ppm). A calculated angle of 83° between the two carbonyl groups suggests that the geometry of **14** is probably similar to that of **5**.

The structure of the η^6 complex **15** is based on the absence of CO ligands, the relatively unperturbed ¹H and ¹³C shifts of the vinyl group (e.g., δ_{13C_α} = 135 ppm, δ_{13C_β} = 115 ppm) and the substantial upfield shift of all of the arene ¹³C resonances (δ 82.3, 83.6, 86.6 and 101$_{ipso}$ ppm). Arene complexes of iron(0) are relatively rare and are generally synthesized by metal atom vapor techniques and from iron(II) chlorides. Examples include (η^6-C₆H₆)FeL₂ (L =

PF₃),[30] P(OCH₃)₃,[31] and P(CH₃)₃.[32] Recently, (η^6-C₆H₅R)Ru(dfepe) (R = H, CH₃, C₆H₁₁) have been prepared by the thermolysis of Ru(dfepe)₂(H)₂ in the corresponding aromatic solvent.[7]

X-ray Structure Determination of 13. The structure of the major product, the η^4-styrene complex **13**, was confirmed by single-crystal X-ray crystallography. Single crystals of **13** were grown from methylene chloride at −30 °C. Complex **13** crystallizes in the triclinic system with space group P1̄. The unit cell contains two molecules separated by the normal van der Waals distances. Crystallographic data are summarized in Table II, while atomic coordinates appear in Table VI. An ORTEP drawing of the

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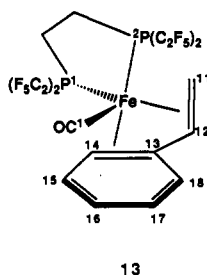
13

molecule is shown in Figure 2, while Table VII lists selected metrical parameters. The geometry around the iron atom can be described as intermediate between trigonal bipyramidal in which the axial ligands are P(2) and the η^2-C_6H_5 moiety and square pyramidal in which the carbonyl ligand occupies the apical position. No significant differences are observed between the two Fe–P bond lengths (2.1364 (13) and 2.1313 (11) Å), and the P(1)–Fe–P(2) angle of 88.3° is similar to that observed in complex 5. The most notable feature of the structure is the very long Fe–C(14) distance of 2.278 (4) Å, which suggests a relatively weak interaction between the C(13)–C(14) double bond and the iron atom. Note also the Fe–C(13) distance (2.159 (3) Å) is considerably longer than the Fe–C(12) length (2.045 (3) Å). (The η^4-styrene derivative, $Fe(CO)_3(\eta^4$-CH(CH$_3$)=C(C$_6$H$_5$)$_2)$, also possesses a long bond between iron and the ortho-carbon of the η^2-bound arene ring (2.230 (8) Å).)[33]

Complex 13 as a Fe(CO)(dfepe)-Transfer Reagent. The weak interaction between iron and the η^2-bound arene in 13 as supported by the X-ray structural results, suggested that the styrene ligand may be quite labile and that 13 may serve as a convenient Fe(CO)(dfepe)-transfer agent. Indeed, this is the case. Treatment of 13 with CO (THF, 25 °C) resulted in the displacement of the η^4-bound styrene and formation of 2. Treatment of 13 with 2 equiv of trimethyl phosphite (THF, 25 °C) results in rapid displacement of styrene and formation of the bis(phosphite) adduct 16. Complex 16 shows only one strong ν_{CO} band at 1944
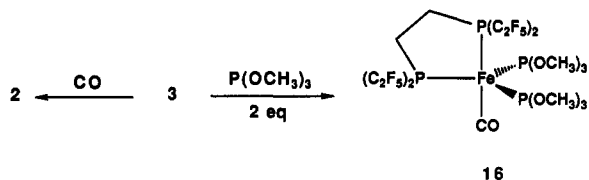
16

cm^{-1}, indicating only one isomer is present rather than two as in the case of $(F_3P)_4Fe(CO)$ which shows two ν_{CO} bands (2037 cm^{-1} CO(axial), 2008 cm^{-1} CO(equatorial)). The ^{31}P NMR spectrum of 16 exhibits a singlet at δ 173 ppm attributed to the phosphite ligands and a septet at δ 132 ppm due to the dfepe ligand. The ^{13}C resonances of the carbonyl ligand appear as a triplet at δ 218.1 ppm ($^2J_{PC} = 26$ Hz) indicating coupling to only two ^{31}P nuclei. An X-ray diffraction study has confirmed the structure of 16 and indicates a slightly distorted trigonal-bypyramidal structure in which CO and one of the dfepe phosphorus atoms occupy the axial positions.[34]

Oxidative Addition Reactions of Photogenerated (dfepe)Fe(CO)$_2$. In view of the fact that 16-electron L$_4$FeO complexes undergo a variety of oxidative addition reactions, including oxidative addition of alkanes, we have investigated oxidative addition reactions of photogenerated (dfepe)Fe(CO)$_2$.

Reaction with H$_2$. Photolysis of complex 2 under a dihydrogen purge in diethyl ether produced the dihydride 17 in a 68% yield. Similar to $Fe(CO)_4(H)_2$, spectroscopic
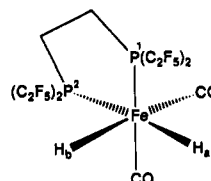
17

data reveal that the dihydride 17 is the classical *cis*-dihydride 17 and not one in which dihydrogen is bound in an η^2 fashion.[35,36] In contrast to $Fe(CO)_4(H)_2$ which is thermally unstable at temperatures above –10 °C, 17 is stable at 45 °C for several hours in solution. Pure 17 decomposes slowly under N$_2$ at –30 °C and must be stored under either Ar or H$_2$.

The ^{1}H NMR spectrum at 25 °C exhibits a 1:2:1 triplet pattern at δ –11.1 ppm with $J_{PH} = 31.4$ Hz. Furthermore, the variable-temperature ^{1}H and ^{31}P spectra show that 17 is stereochemically nonrigid. The 400-MHz ^{1}H NMR spectrum at –84 °C in the high-field region shows two distinct hydride signals at δ –9.5 and –13 ppm. The spectrum observed is consistent only with structure 17 in which the hydride ligands are cis. The observation of two distinct hydride signals clearly suggests a classical dihydride structure for 17 rather than an η^2-H$_2$ structure, since in all previously observed η^2-H$_2$ systems the barriers to H$_2$ rotation are extremely low.[35j,37a,b] The large J_{PH} values are most consistent with terminal hydrides; however, a substantial J_{PH} coupling in an η^2-H$_2$ system has been observed in at least one case.[37c] The signal at δ –9.5 ppm is assigned to H$_a$ on the basis of a large trans coupling $J_{P(2)-H_a} = 63$ Hz and a smaller cis coupling, $J_{P(1)-H_a} = 41$ Hz. The δ –13 ppm signal is assigned to H$_b$ on the basis of two nearly equal cis J_{PH} couplings of 35 and 37 Hz. As the temperature is raised, the two high-field bands broaden and coalesce at –38 °C. From the coalesence equation, $k = \pi(\Delta\nu)/(\sqrt{2})$, the rate constant for site exchange of the two hydrogens is 3.2 × 10^3 s^{-1}, corresponding to $\Delta G^{\ddagger} = 9.9 \pm 0.2$ kcal/mol. The ^{2}H spectrum of (dfepe)Fe(CO)$_2$(D)$_2$ (18) (prepared by photolysis under D$_2$) shows a broad signal at δ –11.1 ppm at 25 °C. The variable-temperature

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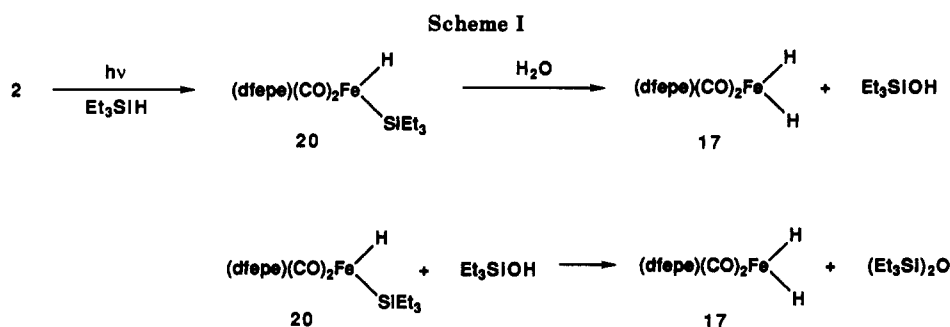(34) Brookhart, M. S.; Chandler, W. A.; White, P. S.; Santini, C. C. Unpublished results.

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Scheme I

$$2 \xrightarrow[\text{Et}_3\text{SIH}]{h\nu} (\text{dfepe})(\text{CO})_2\text{Fe} \overset{\text{H}}{\underset{\text{SIEt}_3}{<}} \xrightarrow{\text{H}_2\text{O}} (\text{dfepe})(\text{CO})_2\text{Fe} \overset{\text{H}}{\underset{\text{H}}{<}} + \text{Et}_3\text{SIOH}$$

$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\text{20} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\text{17}$$

$$(\text{dfepe})(\text{CO})_2\text{Fe} \overset{\text{H}}{\underset{\text{SIEt}_3}{<}} + \text{Et}_3\text{SIOH} \longrightarrow (\text{dfepe})(\text{CO})_2\text{Fe} \overset{\text{H}}{\underset{\text{H}}{<}} + (\text{Et}_3\text{SI})_2\text{O}$$

$$\quad\quad\quad\quad\text{20} \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\text{17}$$

behavior is similar to that of the dihydride but shows a lower T_c (-50 °C) due to the smaller $\nu_{D_a} - \nu_{D_b}$. The rate of site exchange at T_c is calculated as 4.3×10^2 s^{-1}, $\Delta G^{\ddagger}$ = 10.2 ± 0.2 kcal/mol. The data are not sufficiently accurate to estimate k_H/k_D.

The stereochemical nonrigidity of complex 17 is also exhibited in the variable-temperature ^{31}P NMR spectrum. At -35 °C two signals are observed at δ 143 and 133 ppm, which broaden and coalesce at -16 °C. The rate of site exchange at T_c (-16 °C) is calculated as 4×10^3 s^{-1}, $\Delta G^{\ddagger}$ = 10.7 ± 0.3 kcal/mol. In contrast to the tricarbonyl complex 2, the dfepe ligand is quite labile in complex 17. Treatment of 17 with excess trimethyl phosphite in hexanes results in the rapid substitution of the chelating dfepe ligand by 2 molar equiv of trimethyl phosphite to give the known complex $[(\text{CH}_3\text{O})_3\text{P}]_2\text{Fe}(\text{CO})_2(\text{H})_2$[38] (19) in 78% yield. NMR and IR data are consistent with a cis stereochemistry for the H and CO ligands and a trans arrangement for the phosphite ligands. The rate of the substitution reaction under pseudo-first-order conditions (8-fold excess of P(OMe)$_3$) was found to be 7×10^{-3} s^{-1} at -21 °C ($\Delta G^{\ddagger}$ = 17.2 kcal/mol).

Reaction with (C$_2$H$_5$)$_3$SiH. In an attempt to carry out oxidative addition reactions between (dfepe)Fe(CO)$_2$ and silanes, complex 2 was photolyzed in the presence of triethylsilane in a variety of solvents (see Experimental Section). Two major products were isolated, the dihydride complex, 17, and hexaethyldisiloxane, (Et$_3$Si)$_2$O. Even when solvents and glassware were carefully dried, disiloxane was still observed. When this reaction was monitored by GC, triethylsilanol, Et$_3$SiOH, could be detected as an intermediate. We believe formation of 17 and (Et$_3$Si)$_2$O likely involves the reaction sequence shown in Scheme I, in which the silyl hydride, 20, is initially formed but rapidly undergoes the sequence of hydrolysis steps shown. The fact that traces of adventitious water are sufficient to promote formation of 17 suggests that the silyl hydride is extremely reactive toward water. This is likely due to the high stability of the anion, $[(\text{dfepe})(\text{CO})_2\text{FeH}]^-$,[39] which would be the initial product of attack of either water or Et$_3$SiOH on 20. In an attempt to observe the proposed (dfepe)(CO)$_2$Fe(H)(SiR$_3$) intermediate, the reaction was monitored by ^{1}H NMR and IR spectroscopy. No intermediate was observed in the case of triethylsilane, but when diphenylsilane was used, several new features were observed. The ^{1}H NMR spectrum exhibited new resonances at δ 2.74 (PCH$_2$CH$_2$P) and -11.0 (Fe–H) ppm, while the IR spectrum showed new CO-stretching frequencies at 2041 and 2004 cm^{-1}. These new signals are consistent with an iron silyl hydride,[40] (dfepe)(CO)$_2$Fe(H)(SiHPh$_2$),

but attempts to isolate this species gave only 17.

There is substantial precedent for nucleophilic attack at Si and cleavage of Fe–Si bonds in related complexes. For example, Parish[41] has demonstrated that Fe(CH$_2$=CH$_2$)(dppe)$_2$ catalyzes the coupling of primary alcohols, ROH (R = Me, Et, nPr, nBu), with SiH(OEt)$_3$ or SiH$_2$Ph$_2$, to produce ultimately Fe(H)$_2$(dppe)$_2$, Si(OEt)$_n$(OR)$_{4-n}$, and SiPh$_2$(OR)$_2$, respectively. A mechanism for the catalytic process involving the formation of a (dppe)$_2$Fe(H)(SiR$_3$) intermediate followed by nucleophilic attack by alcohol was proposed. It is noteworthy that while Fe(CH$_2$=CH$_2$)(dppe)$_2$ is inactive toward triorganosilanes such as SiH(Et)$_3$ or SiH(Ph)$_3$, 2 readily reacts under photolytic conditions with either substrate. Similarly, Crabtree[42] has proposed a nucleophilic attack by alcohol on an [IrH$_2$-(MeOH)(η^2-HSiEt$_3$)(PPh$_3$)$_2$]$^+$ intermediate in the catalytic alcoholysis of hydrosilanes utilizing [IrH$_2$S$_2$(PPh$_3$)$_2$]SbF$_6$ (S = solvent) as the catalyst. Closely related to the present work is the observation by Schubert[43] that treatment of cis-Fe(CO)$_4$(SiMe$_3$)$_2$ with PPh$_3$ yields (Me$_3$Si)$_2$O, Fe-(CO)$_3$(PPh$_3$)(H)(SiMe$_3$), and other products.

Attempted Oxidative Addition of Alkanes to (dfepe)Fe(CO)$_2$. Highly electron-rich Fe(0) complexes of the type L$_4$Fe (L = phosphine) have previously been observed to undergo oxidative addition reactions with various types of C–H bonds. For example, Ittel and Tolman[44] have demonstrated that upon thermal elimination of naphthalene from HFeNp(dmpe)$_2$ (Np = 2-naphthyl) the coordinatively unsaturated Fe(dmpe)$_2$ intermediate undergoes oxidative addition reactions with aryl C–H bonds and compounds containing activated sp^3 C–H bonds, such as CH$_3$COCH$_3$, CH$_3$CH$_2$CN, and CH$_3$SOCH$_3$. Field[45] further showed that Fe(dmpe)$_2$, generated by photolysis of Fe(H)$_2$(dmpe)$_2$ at -80 °C, activates the sp^3 C–H bonds of pentane and cyclopentane. (The corresponding iron alkyl hydrides, Fe(H)(R)(dmpe)$_2$, are unstable above -30 °C and β-eliminate to form Fe(H)$_2$-(dmpe)$_2$ and olefins.)

Photolysis of 2 in alkane solvents was carried out in an effort to detect either alkane complexes[46] of (dfepe)Fe(CO)$_2$

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(39) The [(dfepe)(CO)$_2$Fe(H)][PPN] complex has been independently synthesized by reacting (dfepe)(CO)$_2$Fe(H)$_2$ with KH in Et$_2$O. IR (Et$_2$O): ν 1947, 1885 cm^{-1}. ^{1}H NMR (THF, 21 °C): δ 7.6 (m, PPN cation, 30 H), 2.1 (m, PCH$_2$CH$_2$P, 4 H), -8.9 (t, Fe–H, $^2J_{PH}$ = 20 Hz, 1 H). ^{13}C NMR: δ 219.6 (s, CO), 120 (m, CF$_2$CF$_3$), 23.75 (m, PCH$_2$CH$_2$P).

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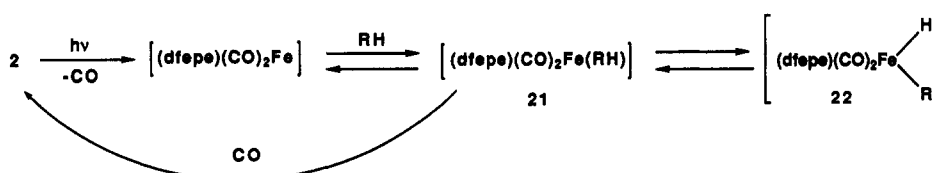
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Scheme II

or oxidative addition adducts (dfepe)(CO)_2Fe(H)(R) and to contrast the behavior of the highly electrophilic unsaturated species (CO)_2Fe(dfepe) with the electron-rich (dmpe)_2Fe system. Irradiation in hexane at 25 and -30 °C resulted in no IR-observable products and only a very slow decrease in intensity of the ν_{CO} bands due to **2**. Additionally, a solution of complex **2** in liquid propane at -50 °C was photolyzed in an NMR tube while being purged with argon. After photolysis, propane was removed under vacuum at -50 °C and CD_2Cl_2 was condensed into the tube at -50 °C. ¹H NMR analysis of the solution at -78 °C showed no new resonances and indicated only the presence of **2**. The efficient photosubstitution of CO in **2** by other ligands such as P(OMe)_3 (see above) clearly indicates that **2** must readily lose CO under these conditions to form (dfepe)(CO)_2Fe. In alkane solutions, rapid recapture of CO must occur before CO can be removed from solution by the argon purge. Similar results have been observed for (dfepe)Cr(CO)_4.[47] The nature of the intermediate (or intermediates) formed in alkane solution is unknown. The possibilities include unsolvated (dfepe)Fe(CO)_2, an alkane complex (dfepe)(CO)_2Fe(RH) (**21**), or the oxidative addition adduct (dfepe)(CO)_2Fe(H)(R) (**22**) (Scheme II). This reaction is currently being examined by laser transient absorption spectroscopy in an effort to address this question.

One feature of significance is the comparison of the photochemistry of **2** with that of the parent carbonyl complex Fe(CO)_5. Whereas photolysis of Fe(CO)_5 in inert solvents leads to rapid cluster formation to yield Fe_2(CO)_9,[48] the bulky dfepe ligand in **2** must prevent such clustering reactions and thus only CO capture occurs and the labile dicarbonyl intermediate(s) returns to **2**.

Experimental Section

General Methods. All reactions were conducted under a dry and oxygen-free argon atmosphere (unless otherwise noted) using Schlenk techniques with a double-manifold vacuum line. Argon and nitrogen gases were purified by passage through a column of BASF catalyst (R3-11) heated to 130 °C followed by activated molecular sieves. Methylene chloride was distilled in an N_2 atmosphere from phosphorus pentoxide prior to use. THF, benzene, toluene, and diethyl ether were distilled in an N_2 atmosphere from sodium and benzophenone prior to use. Solvents for column chromatography were degassed by purging with argon gas for 30 min. Deuterated solvents were used as received. Hexaethyldisilane,[49] (benzylideneacetone)iron tricarbonyl,[27d-e] and 1,2-bis(dichlorophosphino)ethane[50] were prepared as previously described. Glassclad 6C was purchased from Petrarch.

¹H and ¹³C NMR spectra were recorded on Varian XL400 and Bruker AC200 spectrometers in deuterated solvents. When ¹³C data are reported, the following conventions were used: {} indicate proton-decoupled data, () indicate proton-coupled data. ³¹P, ¹⁹F, and ²H NMR spectra were recorded on a Varian XL400 spec-

trometer. Chemical shifts were reported by reference to residues of monoprotio solvents (CHDCl_2, δ 5.32 ppm; C_6HD_5, δ 7.15 ppm; THF-d_7, δ 3.58 ppm). ³¹P and ¹⁹F were referenced externally to 85% H_3PO_4 (δ 0.00 ppm) and C_6H_5CF_3 (δ 0.00 ppm with upfield chemical shifts taken to be negative). Infrared spectroscopy was conducted in solution on a Mattson Polaris FTIR spectrometer using ICON software. GC experiments were conducted on Hewlett-Packard 5890. The columns used were either a 20-ft × ¹/₄-in. column packed with 20% QF-1 on Chromasorb W in conjunction with a thermal detector or an HP ultra 1 (cross-linked methylsilicone gum) capillary column 25-m × 0.2-mm × 0.11-mm film thickness in conjunction with a flame ionization detector. Preparative photolyses were carried out using a reflector flood lamp GE No. HR100PFL44. GC/MS was performed by the UNC-Mass Spectrometry Facility using a VG 70-250 SEQ tandem-hybrid MS/MS system operated in the MS1 (first mass spectrometer only) mode, with data acquisition utilizing a 70-250J data system (DEC-Micro-PDP-11 computer). Elemental analyses were performed by either Galbraith, Inc., Knoxville, TN, or ORS, Inc., Whitesboro, NY.

Synthesis of (C_2F_5)_2PCH_2CH_2P(C_2F_5)_2 (1). Bis(bis(pentafluoroethyl)phosphino)ethane was prepared using a modified literature procedure.[5] A 50-mL aliquot of 2.5 M nBuLi (125 mmol) in hexanes was added to a 500-mL flame-dried Schlenk flask equipped with a mechanical stirrer and a closed-system vacuum adapter (Fischer). The hexanes were removed in vacuo, and 150 mL of freshly distilled anhydrous diethyl ether was added under nitrogen to the butyllithium. Approximately 35.0 g of C_2F_5Cl (bp -34 °C, density ca. 1.88 g/mL, 195 mmol) was condensed into a 50-mL oven-dried Schlenk flask at -78 °C. The butyllithium solution in ether was cooled to -95 °C and the C_2F_5Cl was added very slowly by cannula under nitrogen. (**Caution:** The addition of C_2F_5Cl must be performed slowly. Rapid addition of C_2F_5Cl can result in a rapid pressure buildup.) The reaction mixture was maintained at ca. -95 °C for 1 h. A room-temperature solution of Cl_2PCH_2CH_2PCl_2 (5.75 g, 3.7 mL, 24.8 mmol) in 25 mL of diethyl ether was added slowly by cannula while the reaction mixture was maintained below -90 °C. The mixture was allowed to warm slowly to room temperature (approximately 4-5 h). As the solution temperature increased, the brown solution became dark brown at -70 °C and an extremely viscous white mass formed at 0 °C. The solution was stirred at room temperature for 1 h, after which slightly acidic degassed water (5-10 mL) was added by cannula to the reaction vessel. The mixture was shaken, and the aqueous layer was separated from the ether layer. The organic layer was dried over magnesium sulfate for 1 h and then filtered thru Celite. The diethyl ether was distilled at atmospheric pressure followed by butyl chloride at 67-70 °C. The yellow oil that remained yielded 5-6 g (36-43%) of bis(bis(pentafluoroethyl)phosphino)ethane that was isolated as a clear, colorless liquid upon distillation (55-60 °C/0.14 mmHg, density ca. 1.64 g/mL). ¹H, ¹³C, ³¹P, and ¹⁹F NMR data are similar to those previously reported.[5]

Synthesis of (CO)_3Fe[(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2] (2). To an oven-dried 200-mL flask equipped with a nitrogen inlet tube, a magnetic stirring bar, and a condenser was added 0.87 g (3.1 mmol) of (benzylideneacetone)iron tricarbonyl, 0.9 mL (3 mmol) of bis(bis(pentafluoroethyl)phosphino)ethane, and 100 mL of toluene. The reaction mixture was heated at reflux for approximately 2 h and monitored by IR spectroscopy. At the completion of the reaction, as indicated by the disappearance of the 2068, 2008, and 1989 cm⁻¹ bands and the appearance of bands at 2055, 2004, and 1991 cm⁻¹, the toluene was evaporated under reduced pressure. The product was purified by chromatography on a silica column using hexanes. Following the removal of hexanes under reduced pressure overnight, 1.26 g (59%) of [bis(bis(pentafluoroethyl)phosphino)ethane]iron tricarbonyl was obtained as

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a yellow oil. IR (pentane): ν 2055, 2004, 1919 cm^{-1}. UV (hexane): λ_{max} = 236 and 294 nm. Anal. For C$_{13}$H$_4$F$_{20}$P$_2$O$_3$Fe [found (calcd)]: C, 22.23 (22.19); H, 0.63 (0.57); Fe, 7.37 (7.91). ^{1}H NMR (CD$_2$Cl$_2$, 21 °C): δ 2.6 (m, PCH$_2$CH$_2$P). ^{13}C NMR: δ 22.6 [{t, $^1J_{PC}$ ~ $^2J_{PC}$ ~ 21 Hz}, PCH$_2$CH$_2$P], 120 [{m}, CF$_2$, CF$_3$], 211.2 [{br s}, CO]. ^{31}P NMR: δ 140 (quintet, PCF$_2$CF$_3$). ^{19}F NMR: δ −13.3 (s, CF$_3$), −46.2 (center of the AB part of an ABX system, $^2J_{F_aF_b}$ = 314 Hz, $^2J_{PF_a}$ = 65 Hz, $^2J_{PF_b}$ = 61 Hz, CF$_2$).

Synthesis of (CO)$_2$Fe[(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$](P(OC-H$_3$)$_3$) (4). A solution of 0.4 g (0.6 mmol) of [bis(bis(penta-fluoroethyl)phosphino)ethane]iron tricarbonyl, diethyl ether (30 mL), and a 0.07 mL (0.6 mmol) of trimethyl phosphite was photolyzed at room temperature under argon. The reaction was monitored by IR spectroscopy and judged to be complete as indicated by the disappearance of the bands at 2052, 1999, and 1988 cm^{-1} and the growth of the 1988- and 1937-cm^{-1} bands. The resulting yellow solution was evaporated under reduced pressure and the residue purified by silica column chromatography using a 1:9 dichloromethane:pentane eluent. The solvent was evaporated under reduced pressure to yield 354 mg (79%) of [bis(bis(pen-tafluoroethyl)phosphino)ethane](trimethyl phosphite)iron di-carbonyl as a yellow crystalline material (mp 70–71 °C). IR (pentane): ν 1990, 1940 cm^{-1}. Anal. For C$_{15}$H$_{13}$F$_{20}$P$_3$O$_5$Fe [found (calcd)]: C, 22.89 (22.46); H, 1.62 (1.63); Fe, 6.82 (6.96). ^{1}H NMR (CD$_2$Cl$_2$, 21 °C): δ 2.4 (m, PCH$_2$CH$_2$P, 4 H), 3.8 (d, $^3J_{PH}$ = 12 Hz, P(OCH$_3$)$_3$, 9 H). ^{13}C NMR: δ 22.7 [{t, $^1J_{PC}$ ~ $^2J_{PC}$ ~ 21 Hz}, PCH$_2$CH$_2$P], 54.1 [{s}, OCH$_3$], 120 [{m}, CF$_2$, CF$_3$], 212.1 [{d, $^2J_{PC}$ = 50 Hz}, CO]. ^{31}P NMR: δ 133 (q, $^2J_{PF}$ = 59 Hz, C$_2$F$_5$P), 173 (t, $^2J_{PP}$ = 8 Hz, P(OMe)$_3$). ^{19}F NMR: δ −13.6 (s, CF$_3$), −45.2 (center of the AB part of an ABX system, $^2J_{F_aF_b}$ = 315 Hz, $^2J_{PF_a}$ = 55 Hz, $^2J_{PF_b}$ = 66 Hz, CF$_2$).

Synthesis of (CO)$_2$Fe[(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$](η^2-CH$_2$CH$_2$) (5). [Bis(bis(pentafluoroethyl)phosphino)ethane]iron tricarbonyl (0.2 g, 0.3 mmol) was dissolved in 25 mL of diethyl ether, and the solution was cooled to 0 °C. The solution was purged with ethylene prior to the beginning of photolysis, and a continuous purge was maintained during photolysis. After ca. 2 h, the solution had become darker yellow and the CO bands of the starting material at 2052, 1999, and 1986 cm^{-1} had disap-peared and two new CO bands at 2020 and 1979 cm^{-1} had ap-peared. The solvent was evaporated, and the residue was purified by chromatography on a silica column using hexanes. The first yellow band was collected to yield 0.12 g (60%) of [bis(bis(pen-tafluoroethyl)phosphino)ethane](η^2-ethylene)iron dicarbonyl as a yellow oil after solvent removal. The oil was recrystallized from 2-methylbutane at −30 °C to obtain X-ray-quality single crystals. IR (Et$_2$O): ν 2020, 1979 cm^{-1}. IR (CH$_2$Cl$_2$): ν 2018, 1974 cm^{-1}. Anal. For C$_{14}$H$_8$F$_{20}$P$_2$O$_2$Fe [found (calcd)]: C, 23.78 (23.81); H, 1.42 (1.13). ^{1}H NMR (C$_6$D$_6$, 21 °C): δ 1.7 (m, PCH$_2$CH$_2$P, 4 H), 2.5 (t, CH$_2$=CH$_2$, $^3J_{PH}$ = 3 Hz, 4 H). ^{13}C NMR: δ 21.3 [{t, $^1J_{PC}$ ~ $^2J_{PC}$ ~ 22 Hz}, (t, $^1J_{CH}$ = 140 Hz), PCH$_2$CH$_2$P], 35.6 [{s}, (t, J_{CH} = 160 Hz), CH$_2$=CH$_2$], 120 [{m}, CF$_2$, CF$_3$], 213 [{s}, CO]. ^{31}P NMR: δ 124.3 (m, C$_2$F$_5$P). ^{19}F NMR: δ −18.4 (s, CF$_3$), −49.2 (d, $J_{F_aF_b}$ = 67 Hz, CF$_2$). ^{1}H NMR (CD$_2$Cl$_2$, 21 °C): δ 2.45 (m, PCH$_2$CH$_2$P, 4 H), 2.6 (t, CH$_2$=CH$_2$, $^3J_{PH}$ = 4 Hz, 4 H). ^{13}C NMR: δ 21.7 [{t, $^1J_{PC}$ ~ $^2J_{PC}$ ~ 22 Hz}, PCH$_2$CH$_2$P], 35.6 [{s}, CH$_2$=CH$_2$], 120 [{m}, CF$_2$, CF$_3$], 214 [{s}, CO].

Synthesis of (CO)$_2$Fe[(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$](η^2-CH$_2$CHCH$_3$) (6). The same procedure used in the synthesis of [bis(bis(pentafluoroethyl)phosphino)ethane](η^2-ethylene)iron dicarbonyl was employed for the synthesis of the propylene complex. A 0.2-g (0.3 mmol) sample of [bis(bis(pentafluoro-ethyl)phosphino)ethane]iron tricarbonyl was dissolved in 25 mL of diethyl ether, and the solution was cooled to 0 °C. Propylene was bubbled through the solution prior to the beginning of photolysis. The solution was photolyzed maintaining a vigorous propylene purge, and the reaction was monitored by IR spec-troscopy. After ca. 2 h, the solution had become darker yellow and the CO bands of the starting material at 2052, 1999, and 1986 cm^{-1} had disappeared and two new CO bands at 2013 and 1974 cm^{-1} had appeared. The solvent was evaporated, and the residue was purified by chromatography on a silica column using hexanes. The first yellow band was collected to yield [bis(bis(penta-fluoroethyl)phosphino)ethane](η^2-propylene)iron dicarbonyl as a yellow oil after solvent removal. The propylene complex is thermally unstable and decomposed in CD$_2$Cl$_2$ after ca. 7 h at 25

°C or after ca. 12 h as the neat oil. IR (Et$_2$O): ν 2013, 1974 cm^{-1}. IR (hexane) ν 2017, 1978 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 21 °C): δ 1.7 (s, CH$_3$, 3 H), 1.9–3.2 (overlapping bands due to CH$_2$ propene and PCH$_2$CH$_2$P, 6 H), 4.0 (br, CH, 1 H). ^{13}C NMR: δ 21.5 [{t, $^1J_{PC}$ ~ $^2J_{PC}$ ~ 22 Hz}, (t, $^1J_{CH}$ = 136 Hz), PCH$_2$CH$_2$P], 23.4 [{s}, (q, $^1J_{CH}$ = 129 Hz), CH$_3$], 41.9 [{s}, (t, $^1J_{CH}$ = 154 Hz), CH$_2$], 55.9 [{s}, (d, $^1J_{CH}$ = 154 Hz), CH], 120 [{m}, CF$_2$, CF$_3$], 214 [{s}, CO]. ^{31}P NMR: δ 124.3 (m, C$_2$F$_5$P).

Synthesis of (CO)Fe[(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$](η^4-cyclo-pentadienone) (8). Complex 2 (0.2 g, 0.3 mmol) was dissolved in 25 mL of diethyl ether, and the solution was cooled to 0 °C. Acetylene was bubbled through the solution prior to the beginning of photolysis. The solution was photolyzed maintaining a vigorous acetylene purge, and the reaction was monitored by IR spec-troscopy. After ca. 2 h, the solution had become darker brown, and the CO bands of the starting material at 2052, 1999, 1986 cm^{-1} had disappeared. The solvent was evaporated and the residue dissolved in methylene chloride. The methylene chloride solution was filtered thru Celite, hexanes were added, and the resulting solution was cooled to −30 °C to yield 0.1 g (20%) of [bis(bis-(pentafluoroethyl)phosphino)ethane](η^4-2,4-cyclo-pentadienone)iron monocarbonyl as pale yellow crystals. IR (CH$_2$Cl$_2$): ν 2016, 1646 cm^{-1}. Anal. For C$_{16}$H$_8$F$_{20}$P$_2$O$_2$Fe [found (calcd)]: C, 26.59 (26.31); H, 1.14 (1.09). ^{1}H NMR (CD$_2$Cl$_2$, 21 °C): δ 2.5 (m, PCH$_2$CH$_2$P, 4 H), 4.1 (br, CH, 2 H), 5.33 (br, small coupling of 4 Hz observed, 2 H). ^{13}C NMR: δ 22.9 [{t, $^1J_{PC}$ ~ $^2J_{PC}$ ~ 19 Hz}, PCH$_2$CH$_2$P], 67.2 [{s}, CH], 81.1 [{s}, CH], 119 [{m}, CF$_2$, CF$_3$], 172.6 [{s}, CO(organic)], 212.7 [{s}, CO(metal)].

Synthesis of (CO)Fe[(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$](η^4-CH$_2$CHCHCH$_2$) (9). Complex 2 (0.2 g, 0.3 mmol) was dissolved in 25 mL of diethyl ether, and the solution was cooled to −30 °C. 1,3-Butadiene (ca. 5 mL) was condensed into the flask and the resulting solution purged with a flow of argon. The solution was photolyzed, adding more 1,3-butadiene as needed, and the reaction was monitored by IR spectroscopy. After ca. 1.5 h, the solution had become darker yellow and the CO bands of the starting material at 2052, 1999, and 1986 cm^{-1} had disappeared and one new CO band at 1996 cm^{-1} had appeared. The solvent was evaporated, and the residue was purified by chromatography on a silica column using hexanes. The first yellow band was collected and recrystallized using hexanes at −30 °C to yield 0.07 g (30%) of [bis(bis(pentafluoroethyl)phosphino)ethane](η^4-butadiene)iron monocarbonyl as yellow crystals. IR (Et$_2$O): ν 1996 cm^{-1}. Anal. For C$_{15}$H$_{10}$F$_{20}$P$_2$OFe [found (calcd)]: C, 25.79 (25.59); H, 1.47 (1.43). ^{1}H NMR (C$_6$D$_6$, 21 °C): δ 5.1 (br, (H$_2$, H$_{2'}$) 2 H), 2.1 (br, (H(outer)), 2 H), 1.7 (m, PCH$_2$CH$_2$P, 4 H), 0.05 (br, (H(inner)), 2 H). ^{13}C NMR: δ 22.2 [{t, $^1J_{PC}$ ~ $^2J_{PC}$ ~ 20 Hz}, (t, $^1J_{CH}$ = 137 Hz), PCH$_2$CH$_2$P], 38.7 [{s}, (t, $^1J_{CH}$ = 158 Hz), CH$_2$], 84.8 [{s}, (d, $^1J_{CH}$ = 166 Hz), CH], 119 [{m}, CF$_2$, CF$_3$], 217 [{s}, CO]. ^{31}P NMR: δ 121.9 (m, C$_2$F$_5$P).

Synthesis of (CO)Fe[(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$](η^4-CH$_3$COCHCH$_2$) (10). Complex 2 (0.25 g, 0.35 mmol) was dis-solved in 20 mL of methyl vinyl ketone, and the solution was cooled to 0 °C. The solution was purged with argon prior to the beginning of photolysis. The solution was photolyzed maintaining an argon purge, and the reaction was monitored by IR spec-troscopy. After ca. 5 h, the solution had become blood red and the CO bands of the starting material at 2052, 1999, and 1986 cm^{-1} had disappeared and two new CO bands at 2020 and 1976 cm^{-1} had appeared. The solvent was evaporated, and the residue was purified by chromatography on a silica column using 2-methyl-butane. The first orange band was collected to yield 0.05 g (20%) of [bis(bis(pentafluoroethyl)phosphino)ethane](η^4-methyl vinyl ketone)iron carbonyl as a orange red oil after solvent removal. The oil was recrystallized using 2-methylbutane at −30 °C. IR (Et$_2$O): ν 1976 cm^{-1}. IR (CH$_2$Cl$_2$) ν 1975 cm^{-1}. Anal. For C$_{15}$-H$_{10}$F$_{20}$P$_2$O$_2$Fe [found (calcd)]: C, 24.71 (25.02); H, 1.38 (1.39). ^{1}H NMR (CD$_2$Cl$_2$, 21 °C): δ 5.72 (d of d, $J_{H(2)-H(3)}$ = 5.4 Hz, $J_{H(1)-H(3)}$ = 9 Hz, H$_3$), 2.2 (m, PCH$_2$CH$_2$P, 1 H), 2.65 (m, PCH$_2$-CH$_2$P, 1 H), 2.95 (m, PCH$_2$CH$_2$P, 2 H), 2.45 (s, CH$_3$, 3 H), 1.98 (d, $J_{H(2)-H(3)}$ = 5.4 Hz, H$_2$), 1.38 (t, $J_{H(1)-H(3)}$ = 9 Hz, J_{PH} = 7.8 Hz, H$_1$). ^{13}C NMR: δ 21.0 [{s}, (q, $^1J_{CH}$ = 126 Hz), CH$_3$], 22.2 [{s}, (t, $^1J_{CH}$ = 138 Hz), PCH$_2$CH$_2$P], 23.4 [{s}, (t, $^1J_{CH}$ = 127 Hz), PCH$_2$CH$_2$P], 36.7 [{s}, (t, $^1J_{CH}$ = 161), CH$_2$], 78.5 [{s}, (d, $^1J_{CH}$ = 168 Hz), CH], 119 [{m}, CF$_2$, CF$_3$], 147 [{s}, CO(organic)], 210 [{br s}, CO(metal)].

Photolysis of (CO)$_3$Fe[(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$] with Styrene. Complex 2 (0.3 g, 0.4 mmol) and 10 mL of styrene were dissolved in 150 mL of diethyl ether, and the solution was cooled to 0 °C. The solution was purged with argon prior to the beginning of photolysis. The solution was photolyzed maintaining a vigorous argon purge and the reaction was monitored by IR spectroscopy. After ca. 3 h, the solution had become blood red and the CO bands of the starting material at 2052, 1999, and 1986 cm^{-1} had disappeared and two new CO bands at 2020 and 1982 cm^{-1} had appeared. The solvent was evaporated and the residue was purified by chromatography on a silica column using 2-methylbutane. Three complexes were isolated as described below.

Isolation of (CO)Fe[(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$](η^4-CH$_2$CHC$_6$H$_5$) (13). The first red band was collected and was a mixture of 13 and 15. The residue was recrystallized at –30 °C in methylene chloride to yield 0.15 g (52%) of [bis(bis(pentafluoroethyl)phosphino)ethane](η^4-styrene)iron carbonyl as blood red crystals. See the supplementary section for X-ray data. IR (Et$_2$O): ν 1978 cm^{-1}. Anal. For C$_{19}$H$_{12}$F$_{20}$P$_2$OFe [found (calcd)]: C, 30.48 (30.23); H, 1.67 (1.61). ^{1}H NMR (CD$_2$Cl$_2$, 21 °C) (proton assignments were aided by the use of HETCOR): δ 7.5 (d, CH-(aromatic), J_{PH} = 16 Hz, 1 H), 7.1 (br, CH(aromatic), 2 H), 6.9 (br, CH(aromatic), 1 H), 6.3 (br, H$_{14}$, 1 H), 3.65 (br, H$_{12}$, 1 H), 3.1 (m, PCH$_2$CH$_2$P, 1 H), 2.8 (m, PCH$_2$CH$_2$P, 1 H), 2.2 (m, PCH$_2$CH$_2$P, 1 H), 1.6 (m, PCH$_2$CH$_2$P, 1 H), 1.35 (br, H$_{11}$(outer), 1 H), –0.3 (m, H$_{11}$(inner), 1 H). ^{13}C NMR: δ 22.4 [{t, $^1J_{PC}$ = 17 Hz}, (t, $^1J_{CH}$ = 123 Hz), PCH$_2$CH$_2$P], 23.7 [{t, $^1J_{PC}$ = 22 Hz}, (t, $^1J_{CH}$ = 138 Hz), PCH$_2$CH$_2$P], 35.1 [{s}, (t, $^1J_{CH}$ = 154 Hz), CH$_2$-(vinyl)], 67.5 [{s}, (d, $^1J_{CH}$ = 162 Hz), CH(vinyl)], 70.8 [{s}, (d, $^1J_{CH}$ = 169 Hz), CH(aromatic)], 105.8 [{s}, C(ipso)), 118 [{m}, CF$_2$, CF$_3$], 126.8 [{s}, (d, $^1J_{CH}$ = 161 Hz), CH(aromatic)], 127.3 [{s}, (d, $^1J_{CH}$ = 162 Hz), CH(aromatic)], 129.8 [{s}, (d, $^1J_{CH}$ = 158 Hz), CH-(aromatic)], 137.1 [{s}, (d, $^1J_{CH}$ = 162 Hz), CH(aromatic)], 210.4 [{d, $^1J_{PC}$ = 10 Hz}, CO].

Isolation of (CO)$_2$Fe[(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$](η^2-CH$_2$CHC$_6$H$_5$) (14). The second band to elute (yellow) was collected and the residue recrystallized at –30 °C in hexane to yield [bis(bis(pentafluoroethyl)phosphino)ethane](η^2-styrene)iron dicarbonyl as yellow crystals. IR (hexane): ν 2021, 1983 cm^{-1}. Anal. For C$_{20}$H$_{12}$F$_{20}$P$_2$O$_2$Fe [found (calcd)]: C, 30.32 (30.69); H, 1.56 (1.55). ^{1}H NMR (CD$_2$Cl$_2$, 21 °C): δ 7.2 (br s, CH(aromatic), 5 H), 5.2 (br s, CH(vinyl), 1 H) 1.6–3.3 (m, 5 H), 0.2 (br s, 1 H). ^{13}C NMR: δ 21.6 [{br}, (t, $^1J_{CH}$ = 108 Hz), PCH$_2$CH$_2$P], 32.1 [{s}, (t, $^1J_{CH}$ = 153 Hz), CH$_2$(vinyl)], 57.1 [{s}, (d, $^1J_{CH}$ = 159 Hz), CH(vinyl)], 118 [{m}, CF$_2$, CF$_3$], 126.5 [{s}, (d, $^1J_{CH}$ = 158 Hz), CH(aromatic)], 128.7 [{s}, (d, $^1J_{CH}$ = 160), CH(aromatic)], 143 [{s}, C$_{ipso}$], 213 [{m}, CO]. ^{31}P NMR: δ 125.4 (m, C$_2$F$_5$P).

Isolation of Fe[(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$](η^6-CH$_2$CHC$_6$H$_5$) (15). Complexes 13 and 15 coelute off the column. Complex 15 can be conveniently isolated by reacting a diethyl ether solution of 13 and 15 with excess trimethyl phosphite. The ether solution was stirred under Ar and monitored via IR spectroscopy. At the completion of the reaction, as judged by the disappearance of the 1978-cm^{-1} band and the appearance of a 1934-cm^{-1} band, the solvent was removed under vacuum and the residue was purified by chromatography on a silica column using 2-methylbutane. The first red fraction was collected to yield a red solid after solvent removal under vacuum. The red solid was recrystallized from hexane at –30 °C to yield ca. 5% [bis(bis(pentafluoroethyl)-phosphino)ethane](η^6-styrene)iron as red needles. Anal. For C$_{18}$H$_{12}$F$_{20}$P$_2$Fe [found (calcd)]: C, 30.24 (29.75); H, 1.86 (1.67). ^{1}H NMR (CD$_2$Cl$_2$, 21 °C): δ 6.4 (m, CH(vinyl), 1 H), 5.8–5.3 (m, CH(aromatic), 5 H), 5.2 (m, CH$_2$(vinyl), 1 H) 5.2 (m, CH$_2$(vinyl), 1 H), 2.1 (m, PCH$_2$CH$_2$P, 4 H). ^{13}C NMR: δ 21.6 [{t, $^1J_{PC}$ ~ $^2J_{PC}$ ~ 24 Hz}, (t, $^1J_{CH}$ = 137 Hz), PCH$_2$CH$_2$P], 82.3 [{s}, (d, $^1J_{CH}$ = 169 Hz), CH(aromatic)], 83.6 [{s}, (d, $^1J_{CH}$ = 172 Hz), CH(aromatic)], 86.6 [{s}, (d, $^1J_{CH}$ = 170 Hz), CH(aromatic)], 101 [{s}, C(quaternary aromatic)], 115 [{s}, (t, $^1J_{CH}$ = 155), CH$_2$(vinyl)], 116 [{m}, CF$_2$ CF$_3$], 135 [{s}, (d, $^1J_{CH}$ = 159 Hz), CH(vinyl)]. ^{31}P NMR: δ 112.4 (m, C$_2$F$_5$P).

Synthesis of Fe[(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$](CO)(P(OC-H$_3$)$_3$)$_2$ (16). Complex 13 (0.1 g, 0.2 mmol) and excess trimethyl phosphite were stirred under Ar for 1 h. The reaction was monitored by IR spectroscopy and judged to be complete by the disappearance of the 1978-cm^{-1} band and the appearance of a 1934-cm^{-1} band. The solvent was removed under vacuum, and

the resulting residue was purified by chromatography on silica using two solvent combinations. Hexanes were first eluted down the column in yield two small colored fractions. The solvent was changed to 40% methylene chloride in hexanes, which eluted a bright yellow band. The yellow solution was evaporated and the residue recrystallized from hexanes at –30 °C to yield 70% (0.08 g, 0.09 mmol) of [bis(bis(pentafluoroethyl)phosphino)ethane]-bis(trimethyl phosphite)iron carbonyl as yellow crystals. IR (Et$_2$O): ν 1932 cm^{-1}. Anal. For C$_{17}$H$_{22}$F$_{20}$P$_4$O$_7$Fe [found (calcd)]: C, 22.39 (22.74); H, 2.59 (2.47). ^{1}H NMR (CD$_2$Cl$_2$, 21 °C): δ 2.4 (m, PCH$_2$CH$_2$P, 4 H), 3.65 (s, POCH$_3$, 18 H). ^{13}C NMR: δ 23.3 [{t, $^1J_{PC}$ ~ $^2J_{PC}$ ~ 19 Hz}, PCH$_2$CH$_2$P], 52.8 [{s}, POCH$_3$], 117 [{q of q, $^2J_{FC}$ = 36.6 Hz, $^1J_{FC}$ = 313 Hz}, CF$_3$], 121 [{t of t, $^1J_{FC}$ = 34 Hz, $^1J_{FC}$ = 287 Hz}, CF$_2$], 218 [{t, $^2J_{PC}$ = 24 Hz}, CO]. ^{31}P NMR: δ 132.5 (m, C$_2$F$_5$P), 174.5 (br, (CH$_3$O)$_3$P).

Synthesis of (CO)$_2$Fe[(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$](H)$_2$ (17). A solution of 0.53 g (0.94 mmol) [bis(bis(pentafluoroethyl)-phosphino)ethane]iron tricarbonyl dissolved in 100 mL of diethyl ether was photolyzed at 0 °C during which dihydrogen was purged through the solution. The reaction was monitored via IR spectroscopy and judged to be complete by the disappearance of the 2052-, 1999-, and 1987-cm^{-1} bands and the growth of the 2058- and 2023-cm^{-1} bands. The solvent was evaporated under reduced pressure, and the brownish yellow residue was chromatographed on silica under argon using 2-methylbutane. The first yellow band was collected and the solvent removed in vacuo to yield 0.4 g (68%) of [bis(bis(pentafluoroethyl)phosphino)ethane]dihydridoiron dicarbonyl as a pale yellow oil. The product decomposes very slowly under argon at –30 °C. IR (Et$_2$O): ν 2058 and 2023 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 21 °C): δ 2.5 (m, PCH$_2$CH$_2$P), –11.1 (t, $^2J_{PH}$ = 31 Hz, 2 H), ^{1}H NMR (CD$_2$Cl$_2$, –84 °C): δ –9.5 (dd, $^2J_{P(1)H_a}$ = 41 Hz, $^2J_{P(2)H_a}$ = 63 Hz, H$_a$), –13 (dd, $^2J_{P(1)H_b}$ = 35 Hz, $^2J_{P(2)H_b}$ = 37 Hz, H$_b$). Dynamic NMR: T_c = –38 °C at 400 MHz. T_1 (–80 °C, CD$_2$Cl$_2$) = 275 ms. ^{13}C NMR (21 °C): δ 23.0 [{t, $^1J_{PC}$ ~ $^2J_{PC}$ ~ 18 Hz}, (t, $^1J_{CH}$ = 141 Hz), PCH$_2$CH$_2$P], 120 [{m}, CF$_2$, CF$_3$], 208.2 [{t, $^2J_{PC}$ ~ 4 Hz}, (t, $^2J_{CH}$ = 9 Hz), 2 CO]. ^{31}P NMR (CD$_2$Cl$_2$, 21 °C): δ 137.9 (m). ^{31}P NMR (CD$_2$Cl$_2$, –68 °C): δ 143 (br), 131 (br). Dynamic NMR: T_c = –16 °C at 161 MHz. ^{19}F NMR: δ –13.3 (s, CF$_3$), –47 (center of the AB part of an ABX system, $^2J_{F_aF_b}$ = 300 Hz, $^2J_{PF_a}$ ~ 45 Hz, $^2J_{PF_b}$ = 65 Hz, CF$_2$).

Synthesis of (CO)$_2$Fe[(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$](D)$_2$ (18). [Bis(bis(pentafluoroethyl)phosphino)ethane]dideuterioiron dicarbonyl was synthesized by photolysis of 2 in THF under a D$_2$ purge. Workup was the same as for the dihydride complex 17. After solvent evaporation and chromatography, ^{1}H NMR spectroscopy indicates the presence of the dihydride with an average integration of (methylene:hydride) 10:1. IR (Et$_2$O): ν 2058 and 2020 cm^{-1}. ^{2}H NMR (CH$_2$Cl$_2$, 21 °C): δ –11.14 (m). ^{2}H NMR (CH$_2$Cl$_2$, –79 °C): δ –9.6 (m), –12.9 (m). Dynamic NMR: T_c = –54 °C at 61 MHz.

Photolysis of (CO)$_3$Fe[(C$_2$F$_5$)$_2$PCH$_2$CH$_2$P(C$_2$F$_5$)$_2$] with Et$_3$SiH. The following reaction has been carried out using varying amounts of triethylsilane in diethyl ether as well as neat triethylsilane. All conditions gave the same products and results. Complex 2 (0.2 g, 0.3 mmol) was dissolved in 3 mL of triethylsilane and photolyzed under an Ar atmosphere at 0 °C. The reaction was monitored using IR spectroscopy and GC. IR spectroscopy shows the disappearance of the 2052-, 1998-, and 1986-cm^{-1} bands and appearance of bands at 2057 and 2023 cm^{-1}. The GC conditions were as follows: oven temperature 150 °C, injector temperature 175 °C detector temperature 180 °C, and a flow rate of 50 mL/min (30-ft, packed column). GC shows the growth of a 28.1-min peak, no peaks at higher times. At the completion of the reaction, the crude reaction mixture was separated into two portions. The solvent was evaporated from the first fraction, and the residue was spectroscopically examined by ^{1}H and ^{13}C NMR spectroscopy. The carbonyl-containing species was identified as complex 17 on the basis of comparison to an authentic sample via ^{1}H and ^{13}C NMR and IR spectroscopy. A second product was identified as hexaethyldisiloxane on the basis of comparison to an authentic sample via ^{1}H and ^{13}C NMR analysis. The 28.1-min peak was collected from the second fraction and examined using CI$^+$ and EI$^+$ GC/MS techniques. The mass spectral data were consistent with hexaethyldisiloxane having a 246 isotopic pattern corresponding to [M]$^+$ accompanied by losses of 29 (CH$_2$CH$_3$). Hexaethyldisiloxane was singly injected and also coinjected with

a sample of the crude reaction mixture to confirm its identity as the 28.1-min peak. Hexaethyldisilane appears at 34 min and triethylsilane appears at 2.5 min via GC.

Attempts to rigorously exclude water from the photolysis of complex 2 and triethylsilane included treatment of glassware with Glassclad 6C, flame-drying under vacuum, and distillation of triethylsilane from potassium hydride. Under all conditions formation of hexaethyldisiloxane was noted. Triethylsilanol was identified and found to be present during the photolysis of complex 2, and triethylsilane, by capillary GC, retention time 2.31 min, as compared to the retention times of an authentic sample.

Thermal Reaction of Complex 17 with Trimethyl Phosphite. Synthesis of Dicarbonylbis(trimethyl phosphite)iron Dihydride (19). Complex 17 (0.2 g, 0.3 mmol) and trimethyl phosphite (0.1 g, 0.9 mmol) were dissolved in hexanes. The reaction was monitored by IR spectroscopy and is essentially complete in less than 10 min (25 °C), as indicated by the disappearance of the carbonyl-stretching frequencies at 17 at 2061 and 2028 cm^{-1} and the appearance of two new bands at 2016 and 1974 cm^{-1}. The solvent was evaporated under reduced pressure and the brownish yellow residue was chromatographed on silica using two solvent combinations. Hexanes elute a pale yellow band, complex 2. The solvent was changed to 10% ethyl acetate in hexanes, which eluted a bright yellow band. The yellow solution was evaporated and the residue recrystallized from hexanes at -30 °C in yield 78% (0.1 g, 0.2 mmol) of dicarbonylbis(trimethyl phosphite)]iron dihydride (19) as yellow crystals. IR, ^{1}H, and ^{13}C NMR data are similar to those previously reported.[38]

Kinetics for the Reaction of (CO)$_2$Fe[(C$_2$F$_5$)$_2$PCH$_2$CH$_2$-P(C$_2$F$_5$)$_2$](H)$_2$ (17) and Trimethyl Phosphite. Concentrations of [bis(bis(pentafluoroethyl)phosphino)ethane]dihydrioiron dicarbonyl at any time were determined from absorbance values at 2056 cm^{-1} and a Beer's–Lambert plot derived from five standard [bis(bis(pentafluoroethyl)phosphino)ethane]dihydridoiron dicarbonyl solutions in toluene ranging from 0.367 × 10^{-3} to 5.88 × 10^{-3} M (absorbance = -0.007 + 0.034(concentration) with r = 0.99). Pseudo-first-order rate constants were obtained by plotting ln (concentration) vs time.

Kinetic runs were preformed using a Harrick TFC-M25 temperature-controlled flow-through cell in conjunction with an Omega CN310JC solid-state temperature controller and a Neslab ULT-80DD refrigerated circulating bath. A 3-mL B-D multifit glass syringe equipped with a cooling jacket and a small diagonal hole drilled approximately 0.5 in. from the backend of the syringe was connected to the flow-through cell via a B-D luer lock valve. A [bis(bis(pentafluoroethyl)phosphino)ethane]dihydridoiron dicarbonyl in toluene solution was added to the syringe via the

small hole under an Ar atmosphere, and the resulting solution cooled to -21 °C. Excess neat trimethyl phosphite was added to the syringe via the small hole; the solution was quickly shaken to mix, and injected into the IR cell. Absorbances were taken every 20 s for 10 min ($t_∞$). Two runs were conducted at -21 °C, using 8 equiv of trimethyl phosphite, to give a rate constant of 7 × 10^{-3} s^{-1} (r = 0.96 and r = 0.94) and ΔG^* = 17.2 kcal/mol at -21 °C.

X-ray Structure Determinations. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) using an ω-2θ scan; reflections with $I > 2.5\sigma(I)$ were considered observed and included in subsequent calculations. The structures were solved by direct methods. Refinement was by full-matrix least squares with weights based on counter statistics. Hydrogen atoms were included in the final cycles of refinement in calculated positions with thermal parameters derived from the atom to which they were bonded. Crystal data and experimental conditions are given in Table II. All computations were performed using the NRCVAX suite of programs.[51,52]

Supplementary Material Available: Tables of crystal data and data collection parameters, fractional coordinates of hydrogen atoms, anisotropic thermal parameters, complete bond distances and angles, and torsion angles and additional drawings for 5 and 13 (24 pages); tables listing structure factors for 5 and 13 (36 pages). Ordering information is given on any current masthead page.

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