$R_F = (\sum|F_o| - |F_c|)/\sum|F_o|$; $R_{wF} = (\sum w(|F_o| - |F_c|)^2)/(\sum w|F_o|^2)^{1/2}$.

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Preparation and Isomerism of Bis[μ-(trifluoromethyl)phosphido]-hexacarbonyldiiron, $Fe_2(CO)_6\{\mu\text{-}P(CF_3)(H)\}_2$. Crystal Structure of the Trans Isomer

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Received September 22, 1978

Reaction of $P(CF_3)H_2$ with $Fe_2(CO)_9$ gives $Fe(CO)_4\{P(CF_3)H_2\}$, pyrolysis of which produces bis[μ-(trifluoromethyl)phosphido]-hexacarbonyldiiron, $Fe_2(CO)_6\{\mu\text{-}P(CF_3)(H)\}_2$. The phosphido-bridged dimer exists in two isomeric forms. The trans isomer crystallizes in the triclinic space group $P\bar{1}$, with $a = 8.112$ (2) Å, $b = 8.287$ (3) Å, $c = 12.891$ (2) Å, $\alpha = 79.56$ (1)°, $\beta = 80.88$ (1)°, and $\gamma = 69.52$ (2)°. The structure has been determined from 1906 X-ray counter intensities by Patterson and Fourier techniques and refined by full-matrix least-squares methods to $R = 7.40\%$ (9.32% weighted). There is a direct interaction between the axial CF_3 group and the axial H atom, seen both in the crystal structure and in the ^{19}F NMR spectrum of a solution in CCl_3F.

Introduction

The reaction of phosphines (L) with $Fe(CO)_5$ normally results in the simple substitution of one or more carbonyl groups by L. Complexes $Fe(CO)_4L$ can also be prepared by the reaction of L with $Fe_2(CO)_9$.[2] $P(CF_3)_2H$, however, reacts with $Fe(CO)_5$ to give two phosphido-bridged species $H_2Fe_2(CO)_6\{\mu\text{-}P(CF_3)_2\}_2$ and $Fe_2(CO)_6\{\mu\text{-}P(CF_3)_2\}_2$ and with $Fe_2(CO)_9$ to give $Fe(CO)_4\{P(CF_3)_2H\}$, thermolysis of which yields the same two bridged complexes.[3]

We have investigated the reaction of $P(CF_3)H_2$ with $Fe_2(CO)_9$ and find that a simple substitution product, $Fe(CO)_4\{P(CF_3)H_2\}$, and a phosphido-bridged complex, $Fe_2(CO)_6\{\mu\text{-}P(CF_3)H\}_2$, can be prepared. The latter exists in two isomeric forms.

Experimental Section

Volatile compounds were handled in a Pyrex vacuum system. Air-sensitive solids and solutions were protected by an atmosphere of nitrogen. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer and calibrated against CO. Mass spectra were obtained with an AEI MS9 instrument operating at an ionizing energy of 70 eV. NMR spectra were recorded on a Brucker Spectrospin HFX machine operating at 90 MHz for ^1H and 84.66 MHz for ^{19}F nuclei. (Trifluoromethyl)phosphine, $P(CF_3)H_2$, was prepared by the literature method.[4]

Reaction of $Fe_2(CO)_9$ with $P(CF_3)H_2$. $Fe_2(CO)_9$ (0.96 mmol) and excess $P(CF_3)H_2$ (2.46 mmol) were sealed in a small tube (5 cm³). After 6 days at 21 °C, vacuum fractionation of the volatile products gave $P(CF_3)H_2$ (1.45 mmol), $Fe(CO)_5$ (0.84 mmol), and ((trifluoromethyl)phosphine)tetracarbonyliron, $Fe(CO)_4\{P(CF_3)H_2\}$ (0.61 mmol, 64%). Calcd for $C_5H_2F_3FeO_4P$: Fe, 20.7; *m/e* 269.8992. Found: Fe, 20.9; *m/e* 269.8986. The complex is an orange-brown liquid with a vapor pressure of ca. 1 mmHg at 20 °C.

Table I. Crystal Data

	isomer A	isomer B
space group	$P\bar{1}$	$P2_1/c$
a, Å	8.112 (2)	17.20 (1)
b, Å	8.287 (3)	11.41 (1)
c, Å	12.891 (2)	14.91 (2)
α, deg	79.56 (1)	
β, deg	80.88 (1)	92.57 (7)
γ, deg	69.52 (2)	
U, Å³	794.1	2924
d_{calcd}, g cm⁻³	2.02	2.19
Z	2	8
mol wt	481.7	481.7
F(000)	468	1872
radiation	Mo Kα	Mo Kα
λ, Å	0.710 69	0.710 69
μ, cm⁻¹	21.66	23.48

Pyrolysis of $Fe(CO)_4\{P(CF_3)H_2\}$. A pure sample (1.33 mmol) was heated to 70 °C for 7 days in a small sealed tube. The volatile products were noncondensable gas (27% H_2, 70% CO by mass spectroscopy) and small amounts (ca. 0.2 mmol each) of $P(CF_3)H_2$, $Fe(CO)_5$, and $Fe(CO)_4\{P(CF_3)H_2\}$, identified by IR and NMR spectroscopy. The residue in the tube was a red oily material, from which a lemon-colored crystalline solid, mp 92–95 °C, could be sublimed by continuous pumping at room temperature. Resublimation at 40 °C gave pure bis[μ-(trifluoromethyl)phosphido]-hexacarbonyldiiron, $Fe_2(CO)_6\{\mu\text{-}P(CF_3)H\}_2$ (0.13 mmol, 20%). Calcd for $C_8H_2F_6Fe_2O_6P_2$ *m/e* 481.7927; found *m/e* 481.7932. No other pure species could be obtained from the residue; its NMR spectrum contained no signals corresponding to hydrogen bonded directly to iron.

The ^{19}F and ^1H NMR spectra of the dimer were recorded for solutions in CCl_3F, $(CD_3)_2CO$, and CH_3CN. The IR spectrum was obtained from a solution in CH_2Cl_2. No separation of isomers was achieved by fractional sublimation, fractional crystallization, or column chromatography.

Examination of Crystals. The crystals produced by sublimation were of generally poor quality and were irregular in shape. With a microscope it was possible to distinguish two types of crystals, one rather darker than the other. A number of crystals of each type were examined, both by optical means and by X-ray precession photography. Crystal data are summarized in Table I. The densities were not measured, because the crystals dissolved rapidly in all liquids tried. The unit cell dimensions were obtained by a least-squares refinement based on observed and calculated positions of spots on the photographs, and those for the darker crystals (isomer A) were subsequently refined along with the orientation matrix for a crystal mounted on a Hilger-Watts *Y* 290 four-circle diffractometer, from the setting angles at room temperature of 12 reflections with $35° < 2\theta < 49°$ (Mo Kα radiation, λ 0.710 69 Å).[5] There were no systematic absences for isomer A. Those for isomer B (*h*0*l* for *l* odd; 0*k*0 for *k* odd) specify the space group uniquely as $P2_1/c$, and there must be two crystallographically independent molecules in the asymmetric unit.

Collection of Intensity Data. No crystals of isomer B were of adequate quality for intensity data collection. A plate crystal of isomer A was sealed in a Lindemann glass tube and mounted on the diffractometer with the ϕ axis approximately bisecting *b* and *c*.

Intensities were collected by θ–2θ scans at room temperature. A peak sampling routine was used, with a 1-s count at the calculated peak position and at a background position, a full scan being subsequently made only if the net intensity $I' > 2\sigma(I')$. The scan range was 0.72° at low θ, increasing to 0.88° at $2\theta = 50°$ to allow for α_1–α_2 splitting; a 2-s count was made every 0.01°, and two background counts, each one-quarter of the total scan time, were made at the ends of the scan range. All independent reflections with $2\theta \leq 50°$ were sampled, and 2055 were measured by a full scan. A total of 149 had $I < 3\sigma(I)$ and were omitted from the data. For the remaining 1906 independent reflections, corrections were made for *Lp* factors, crystal decomposition (less than 2% during the data collection, according to the periodic measurement of three standard reflections), and absorption.[6] The absorption corrections were of the Gaussian integration type ($\mu = 21.66$ cm^{-1}, 384 grid points); the crystal was measured with a traveling microscope and was approximated by six faces ($01\bar{2}$, $0\bar{1}2$, 100, $\bar{1}00$, 021, $0\bar{2}\bar{1}$) at 0.25, 0.25, 0.25, 0.25, 0.075, and 0.075 mm, respectively, from the center of the crystal. Intensities and estimated standard deviations were derived as reported previously.[7]

The centrosymmetric space group $P\bar{1}$ was assumed and was confirmed by successful refinement.

Structure Solution and Refinement. The nonhydrogen atoms were located by Patterson and Fourier syntheses, and parameters were refined by full-matrix least-squares methods. Scattering factors for uncharged atoms, including corrections for anomalous scattering, were taken from ref 8. The quantity minimized was $\sum w\Delta^2$, with $\Delta = F_o - F_c$ and $w^{-1} = \sigma^2(F_o) + gF_o^2$. The parameter *g* was optimized during refinement to make the indicator $V (=\{\sum w\Delta^2/\sum w\}^{1/2})$ independent of F_o; the final value of *g* was 0.0115.

The axial CF_3 group was found to be disordered: a simple model of two orientations with occupation factors included in the refinement proved adequate.

With anisotropic thermal parameters for all atoms, R $(=\sum|\Delta|/\sum|F_o|)$ and R_w $(=\{\sum w\Delta^2/\sum wF_o^2\}^{1/2})$ were 7.66 and 9.63%, respectively. At this stage, the two hydrogen atoms were located in a difference synthesis. They were assigned isotropic thermal parameters. Further refinement reduced *R* to 7.42% and R_w to 9.31%. Although the refined position of the axial hydrogen atom was reasonable, that for the equatorial atom was somewhat removed from the approximate plane of the two C–P–H groups, which bisects the $(OC)_3Fe$–$Fe(CO)_3$ unit, and esd's for this atom were rather high, indicating poor determination of the equatorial hydrogen atom position by the diffraction data [the two Fe–P(1)–H(1) angles were 135 (10) and 91 (9)°, whereas the Fe–P(2)–H(2) angles were 125(2) and 124 (2)°; P(1)–H(1) was 1.23 (19) Å and P(2)–H(2) was 1.67 (6) Å]. Constraints were, therefore, applied to the hydrogen atom positions during refinement. Of various sets of constraints tested, the one finally chosen, on the ground that it was simple, effective, and reasonable, involved fixing the two P–H bond lengths at 1.40 Å[9] and constraining the two Fe···H(1) distances to be equal and the two Fe···H(2) distances to be equal. Since the four Fe–P bond lengths are virtually equal, this effectively constrains the two hydrogen atoms to lie approximately in the bisecting plane of the molecule. After several cycles of refinement with these constraints, the final values of *R* and R_w were 7.40 and 9.32%. The largest shift:esd ratio for the atomic coordinates in the last cycle was 0.10 and, for the thermal parameters, 0.08, except for atoms in the disordered CF_3 group, which had shifts up to 0.41 and 0.68 times the esd. *V*, the root-mean-square deviation of a reflection of unit weight on an absolute scale of F_c, was 1.33 electrons and showed no systematic trends as a function of indices, sin θ, or F_o. A comparison of F_o and F_c for strong, low-angle reflections indicated no noticeable extinction effects. A final difference synthesis showed no peaks larger than 1.5 e Å^{-3}, the largest being close to the heaviest atoms, and no significant features around the hydrogen and disordered fluorine atoms. Inclusion of the 149 "unobserved" reflections gave values of 7.74 and 9.74% for *R* and R_w: there were no significantly large values of Δ for these reflections.

Table II. Atomic Coordinates ($\times 10^4$)[a]

atom	*x*	*y*	*z*
Fe(1)	2100 (2)	2231 (2)	3436 (1)
Fe(2)	1211 (1)	930 (2)	1950 (1)
C(11)	9 (13)	3569 (13)	4013 (8)
O(11)	−1328 (11)	4402 (13)	4360 (7)
C(12)	3557 (12)	3258 (12)	3753 (7)
O(12)	4472 (10)	3886 (10)	3944 (7)
C(13)	2221 (13)	598 (14)	4565 (8)
O(13)	2228 (13)	−418 (12)	5294 (6)
C(21)	−1148 (13)	1825 (13)	2048 (8)
O(21)	−2655 (10)	2400 (13)	2102 (7)
C(22)	1679 (13)	552 (15)	598 (9)
O(22)	1999 (13)	302 (15)	−257 (7)
C(23)	1052 (14)	−1080 (14)	2625 (9)
O(23)	930 (12)	−2392 (11)	3076 (9)
P(1)	1241 (3)	3582 (3)	1891 (2)
P(2)	3879 (3)	409 (3)	2382 (2)
C(1)	2614 (17)	4564 (16)	837 (9)
F(11)	4101 (33)	3452 (35)	490 (21)
F(12)	2585 (108)	4185 (87)	−56 (22)
F(13)	1871 (39)	5258 (72)	−8 (26)
F(14)	1928 (48)	6241 (26)	677 (41)
F(15)	3183 (57)	5680 (52)	1150 (19)
F(16)	4181 (31)	4093 (68)	993 (35)
C(2)	5336 (15)	−1810 (15)	2873 (11)
F(21)	5872 (13)	−2846 (10)	2144 (8)
F(22)	4569 (12)	−2589 (10)	3674 (7)
F(23)	6797 (12)	−1751 (12)	3185 (10)
H(1)	−297 (48)	5031 (45)	1795 (41)
H(2)	5186 (91)	839 (121)	1653 (23)

[a] In this and subsequent tables, estimated standard deviations in the last place of figures are given in parentheses.

Refinement based on data uncorrected for absorption led to values for *R* and R_w of 7.57 and 9.52%.

Observed and calculated structure factors on an absolute scale (electrons) and anisotropic thermal parameters are available as supplementary material. Structural results are given in the tables: atomic coordinates in Table II, bond lengths and angles in Table III, and selected planes through atomic positions in Table IV.

Results and Discussion

The monosubstituted complex $Fe(CO)_4\{P(CF_3)H_2\}$ was obtained in high yield when $Fe_2(CO)_9$ was treated with an excess of $P(CF_3)H_2$ at room temperature. No reaction occurred, however, unless the pressure of $P(CF_3)H_2$ was high enough to ensure that at least some of the phosphine was in the liquid phase.

In trigonal-bipyramidal complexes of the formula $Fe(CO)_4L$, the phosphine L is normally found in the axial position,[10] but both axially and equatorially substituted isomers are present in significant amounts when highly electronegative substituents (e.g., F) are attached to phosphorus.[11] $Fe(CO)_4\{P(CF_3)H_2\}$ gives a seven-line infrared spectrum in the carbonyl region [ν (cm^{-1}): 2080 (m), 2074 (m), 2023 (s), 1999 (vs) (asymmetrical, indicating partial resolution of two overlapping bands), 1984 (vs), 1972 (s, shoulder); *n*-hexane solution], demonstrating the presence of both isomers. The ^1H and ^{19}F NMR spectra both showed just one resonance [τ_H

Table III

	Bond Lengths, Å		
Fe(1)-Fe(2)	2.661 (2)	C(12)-O(12)	1.122 (11)
Fe(1)-P(1)	2.189 (3)	C(13)-O(13)	1.142 (12)
Fe(1)-P(2)	2.192 (3)	C(21)-O(21)	1.142 (12)
Fe(2)-P(1)	2.194 (3)	C(22)-C(22)	1.131 (13)
Fe(2)-P(2)	2.195 (2)	C(23)-O(23)	1.165 (13)
Fe(1)-C(11)	1.801 (10)	C(1)-F(11)	1.306 (25)
Fe(1)-C(12)	1.809 (9)	C(1)-F(12)	1.253 (29)
Fe(1)-C(13)	1.788 (11)	C(1)-F(13)	1.273 (23)
Fe(2)-C(21)	1.787 (10)	C(1)-F(14)	1.294 (23)
Fe(2)-C(22)	1.785 (11)	C(1)-F(15)	1.314 (18)
Fe(2)-C(23)	1.771 (10)	C(1)-F(16)	1.231 (26)
P(1)-C(1)	1.871 (10)	C(2)-F(21)	1.309 (15)
P(2)-C(2)	1.864 (12)	C(2)-F(22)	1.305 (15)
C(11)-O(11)	1.135 (12)	C(2)-F(23)	1.330 (14)
	Bond Angles, Deg		
Fe(2)-Fe(1)-C(11)	103.7 (3)	Fe(1)-Fe(2)-C(21)	104.1 (4)
Fe(2)-Fe(1)-C(12)	146.1 (3)	Fe(1)-Fe(2)-C(22)	144.6 (3)
Fe(2)-Fe(1)-C(13)	103.5 (3)	Fe(1)-Fe(2)-C(23)	102.7 (3)
Fe(2)-Fe(1)-P(1)	52.7 (1)	Fe(1)-Fe(2)-P(1)	52.5 (1)
Fe(2)-Fe(1)-P(2)	52.7 (1)	Fe(1)-Fe(2)-P(2)	52.6 (1)
P(1)-Fe(1)-C(11)	86.9 (3)	P(1)-Fe(2)-C(21)	87.5 (3)
P(1)-Fe(1)-C(12)	105.7 (3)	P(1)-Fe(2)-C(22)	104.2 (4)
P(1)-Fe(1)-C(13)	154.1 (3)	P(1)-Fe(2)-C(23)	153.2 (4)
P(1)-Fe(1)-P(2)	79.1 (1)	P(1)-Fe(2)-P(2)	78.9 (1)
P(2)-Fe(1)-C(11)	156.4 (3)	P(2)-Fe(2)-C(21)	156.6 (4)
P(2)-Fe(1)-C(12)	101.8 (3)	P(2)-Fe(2)-C(22)	101.3 (3)
P(2)-Fe(1)-C(13)	94.1 (3)	P(2)-Fe(2)-C(23)	93.9 (3)
C(11)-Fe(1)-C(12)	100.2 (4)	C(21)-Fe(2)-C(22)	100.4 (5)
C(11)-Fe(1)-C(13)	90.2 (5)	C(21)-Fe(2)-C(23)	89.7 (5)
C(12)-Fe(1)-C(13)	100.1 (5)	C(22)-Fe(2)-C(23)	102.5 (5)
Fe(1)-C(11)-O(11)	178.4 (10)	Fe(2)-C(21)-O(21)	179.4 (10)
Fe(1)-C(12)-O(12)	179.4 (9)	Fe(2)-C(22)-O(22)	179.1 (10)
Fe(1)-C(13)-O(13)	177.3 (10)	Fe(2)-C(23)-O(23)	179.2 (10)
Fe(1)-P(1)-Fe(2)	74.8 (1)	Fe(1)-P(2)-Fe(2)	74.7 (1)
Fe(1)-P(1)-C(1)	124.3 (4)	Fe(1)-P(2)-C(2)	123.2 (4)
Fe(1)-P(1)-H(1)	122.1 (21)	Fe(1)-P(2)-H(2)	121.7 (30)
Fe(2)-P(1)-C(1)	122.6 (4)	Fe(2)-P(2)-C(2)	122.9 (4)
Fe(2)-P(1)-H(1)	121.8 (21)	Fe(2)-P(2)-H(2)	121.6 (30)
C(1)-P(1)-H(1)	94.4 (30)	C(2)-P(2)-H(2)	95.4 (43)
P(1)-C(1)-F(11)	114.4 (13)	P(1)-C(1)-F(12)	111.6 (17)
P(1)-C(1)-F(13)	113.9 (13)	P(1)-C(1)-F(14)	111.4 (14)
P(1)-C(1)-F(15)	114.4 (11)	P(1)-C(1)-F(16)	113.6 (14)
F(11)-C(1)-F(13)	102.6 (24)	F(12)-C(1)-F(14)	101.1 (30)
F(11)-C(1)-F(15)	101.1 (18)	F(12)-C(1)-F(16)	106.5 (33)
F(13)-C(1)-F(15)	109.1 (22)	F(14)-C(1)-F(16)	111.8 (24)
P(2)-C(2)-F(21)	112.8 (9)	F(21)-C(2)-F(22)	106.4 (10)
P(2)-C(2)-F(22)	113.0 (8)	F(21)-C(2)-F(23)	105.7 (10)
P(2)-C(2)-F(23)	111.0 (9)	F(22)-C(2)-F(23)	107.3 (12)

Table IV. Equations of Planes through Atomic Positions, Referred to an Orthogonal Angstrom Coordinate System with X along a^* and Z along c

plane	atoms	equation
1	Fe(1), P(1), P(2)	$0.6687X + 0.7354Y + 0.1096Z = 3.3596$
2	Fe(2), P(1), P(2)	$-0.3576X - 0.1351Y + 0.9241Z = 2.1226$
3	Fe(1), Fe(2), P(1)	$0.9506X + 0.0364Y - 0.3083Z = 0.0435$
4	Fe(1), Fe(2), P(2)	$0.0941X + 0.8477Y - 0.5221Z = 0.4659$

planes	dihedral angle, deg	planes	dihedral angle, deg
1-2	103.7	3-4	106.3

= 4.57, δ_F = 55.5 (relative to CCl_3F solvent, $^2J_{PF}$ = 69 Hz, $^3J_{FH}$ = 7.9 Hz, $^1J_{PH}$ = 355 Hz], and the ^{19}F spectrum was independent of temperature between −90 and +24 °C. The interconversion of the two isomers is, then, rapid on the NMR time scale.

Pyrolysis of $Fe(CO)_4\{P(CF_3)H_2\}$ gave a yellow crystalline dimer of formula $Fe_2(CO)_6\{P(CF_3)H\}_2$, together with gaseous hydrogen. No species $H_2Fe_2(CO)_6\{P(CF_3)H\}_2$ was detected,

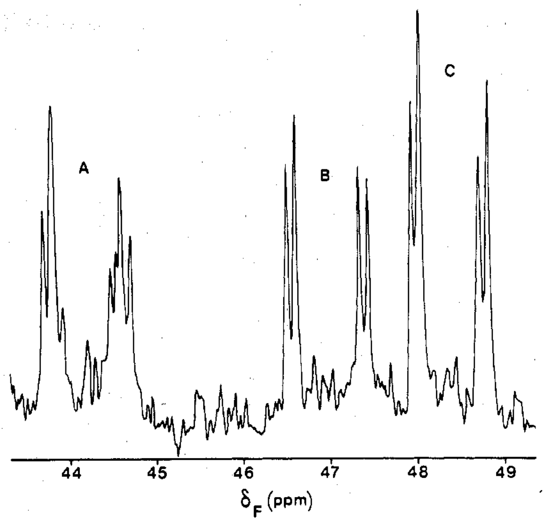
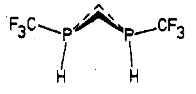


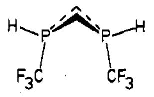
Figure 1. ^{19}F NMR spectrum of a CCl_3F solution of $Fe_2(CO)_6\{\mu\text{-}P(CF_3)(H)\}_2$.

in contrast to the results of pyrolysis of $Fe(CO)_4\{P(CF_3)_2H\}$,[3] though such a species is likely to be an intermediate in the pyrolysis.

If one assumes a folded Fe_2P_2 ring for the dimer, three isomeric forms (**1**, **2**, and **3**) are possible, differing only in the



1



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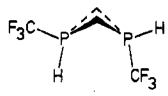

3

relative position of H and CF_3 substituents on phosphorus. The cis isomers **1** and **2** can be interconverted by a simple inversion of the Fe_2P_2 ring, but the trans isomer **3** cannot be converted into either of the other forms without breaking bonds. The cis diaxial isomer **2** is likely to be sterically less stable than the cis diequatorial **1**.

The ^{19}F NMR spectrum contains three resonances (Figure 1). Resonances A and C are of equal intensity and are assigned to the axial and equatorial CF_3 groups, respectively, of isomer **3**. A (δ_F = 44.2) shows, in addition to the expected $^2J_{PF}$ and $^3J_{FH}$ couplings (63 and 8 Hz, respectively), a further coupling of 9 Hz, which is interpreted as $^5J_{FH}$, arising from a weak through-space interaction between the axial CF_3 and H substituents. C has δ_F = 48.3, $^2J_{PF}$ = 62 Hz, $^3J_{HF}$ = 7.5 Hz. Resonance B (δ_F = 47.0, $^2J_{PF}$ = 67 Hz, $^3J_{HF}$ = 7.5 Hz) is attributed to isomer **1**, and the ratio of **3**:**1** is about 5:2. Isomer **2** is not detected; no resonance attributable to it could be separated out from A, B, or C by the use of other solvents.

The ^{19}F NMR spectrum should be temperature dependent, as found for $Fe_2(CO)_6\{P(CF_3)_2\}_2$,[12] with A and C collapsing to a multiplet resonance at higher temperature, as ring inversion becomes rapid on the NMR time scale. This could not be observed, however, as traces of paramagnetic precipitates were deposited at higher temperatures, leading to loss of signal.

Only a single broad resonance at τ = 6.2 was observed in the ^1H NMR spectrum. This suggests that proton exchange is slow enough for $^3J_{FH}$ to be detected in the ^{19}F NMR spectrum but too fast for the resolution of individual environments of the protons. This is reasonable, since $^1J_{PH}$ would be around 350 Hz, much larger than $^3J_{FH}$.

The infrared spectrum has five bands [ν (cm^{-1}): 2093 (w), 2090 (vw, sh), 2057 (vs), 2024 (s, sh), 2020 (s); CH_2Cl_2 solution], with some variation of the relative intensities of the bands at 2024 and 2020 cm^{-1} with concentration.

Examination of crystals with a microscope allows separation into two types, presumably crystals of isomer 1 and of isomer

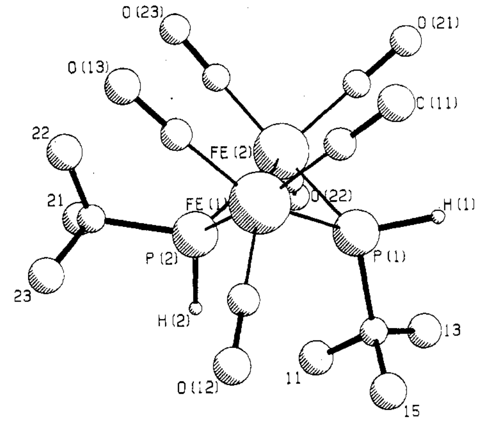

Figure 2. Perspective view of a molecule of the trans isomer. Only one component of the disordered axial CF_3 group is shown. The fluorine atoms are labeled by number only; carbon atom labels are omitted.

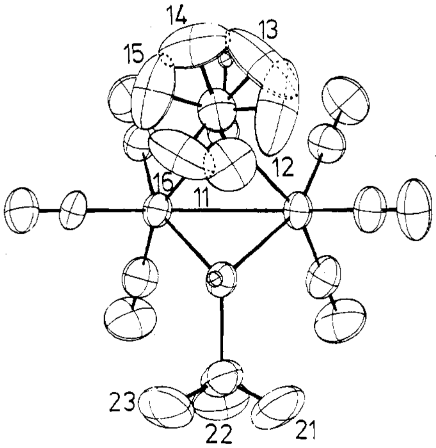

Figure 3. Thermal motion depicted as 40% probability ellipsoids. The fluorine atoms are labeled. Both disorder components are shown.

3, since one type of crystal is shown by X-ray crystallography (vide infra) to be of isomer **3**. If crystals of either of these types are dissoved in CH_2Cl_2, the infrared spectrum is identical with that above, indicating that the isomers interconvert in solution, either by inversion at phosphorus during proton exchange or by breaking and re-forming bonds other than P–H.

The darker, triclinic crystals of the dimer are shown, by X-ray diffraction, to be of the trans isomer **3**. A perspective view of one molecule is shown in Figure 2, and Figure 3 displays the thermal motion and the disorder of the axial CF_3 group. The two components of the disorder have essentially equal site occupancy, the occupancy factor for F(11), -(13), and -(15) being 56 (5)%, and correspond to rotation of the axial CF_3 group about the C–P bond by approximately +16 or −34° from a position in which one fluorine atom would lie equidistant from the two iron atoms and the whole CF_3 group would conform to the approximate $C_s(m)$ symmetry of the rest of the molecule.

Fe–C and C–O bond lengths are typical of those in iron carbonyl complexes. The metal–carbonyl groups are all essentially linear.

There are no unusual intermolecular interactions and the packing is governed by normal van der Waals contacts.

The ^{19}F NMR evidence for a direct through-space H···F interaction is borne out by the observed structure. H(2)···F(11) and H(2)···F(16) are 2.37 and 2.55 Å, respectively. The high thermal motion of the disordered CF_3 group produces systematically low C–F bond lengths and, hence, artificially high values for these two H···F distances, so it is likely that there is a significant interaction..

We have previously reported[7] the molecular structure of the complex containing bridging $P(CF_3)_2$ instead of $P(CF_3)(H)$. Compared with other related PR_2-bridged molecules,[7,13] it was found to have a considerably longer Fe–Fe distance, shorter Fe–P, wider Fe–P–Fe angle and a larger flap angle between the two Fe_2P planes. These differences are in accord with isovalent hybridization arguments[14] and with simple molecular orbital calculations.[15]

The present structure has an average Fe–P bond length of 2.193 Å, very similar that of the $P(CF_3)_2$-bridged complex, but the geometry of the Fe_2P_2 core of the molecule otherwise resembles more closely that of the other complexes in the PR_2-bridged series. There are two obviously possible explanations for this: (i) the steric effect of the CF_3 substituents is larger than previously thought and causes the $P(CF_3)_2$-bridged complex to be anomalous; (ii) the F···H interaction has a significant effect on the molecular geometry, producing a greater folding of the Fe_2P_2 ring, in opposition to the electronic, and possibly steric, effect of the CF_3 substituents. We are unable at present to assess these two possibilities.

Acknowledgment. The authors thank Drs. R. C. Dobbie and J. K. Burdett for advice and Dr. H. M. M. Shearer for assistance in the X-ray data collection. Calculations were performed on the Newcastle University IBM370/168 and Hewlett-Packard 2000E computers. Gratitude is expressed to the Science Research Council for a maintenance grant to S.M.

Registry No. $Fe_2(CO)_6\{\mu\text{-}P(CF_3)H\}_2$ (isomer **3**), 69256-61-7; $Fe_2(CO)_6\{\mu\text{-}P(CF_3)H\}_2$ (isomer **1**), 69204-57-5; $Fe(CO)_4\{P(CF_3)H_2\}$, 69204-56-4; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Listings of structure factor amplitudes and anisotropic thermal parameters (10 pages). Ordering information is given on any current masthead page.

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