Inorg. Chem. **1986**, *25*, 4751–4755

Contribution from the Department of Chemistry, University of Southern California,
Los Angeles, California 90089-1062

Tris(trifluoromethyl)phosphine Iron(0) Carbonyls: Stereochemical Effects

Anton B. Burg

Received April 3, 1986

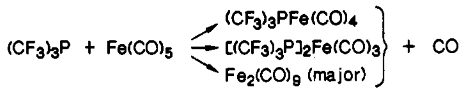
The displacement of CO from $Fe(CO)_5$ by $(CF_3)_3P$ (in sunlight) stops at the third stage, forming the relatively inert complex $[(CF_3)_3P]_3Fe(CO)_2$ ("P-3", mp 90 °C) preceded by $[(CF_3)_3P]_2Fe(CO)_3$ ("P-2", mp −23 °C) and $(CF_3)_3PFe(CO)_4$ ("P-1", mp 45 °C). At first, much $Fe_2(CO)_9$ appears; heating it (in the dark) with $(CF_3)_3P$ gives P-1 but less P-2. The synthesis of P-2 lacks efficiency because it disproportionates to P-1 and P-3, with side reactions irreversibly forming polyiron material. However, P-2 with excess $(CF_3)_3P$ goes to P-3 with minor P-1 and minimal nonvolatiles, for a quantitative account of the P-3 synthesis. PF_3 reversibly displaces $(CF_3)_3P$ and CO from P-2, giving a complicated mixture. X-ray crystallography (by standard methods) on one P-3 crystal confirmed that all three P atoms are equatorial on the trigonal bipyramid about iron. The space group is $P6_3$ (No. 173), with a unit cell containing two molecules: $V = 1267$ (2) Å^3; $a = b = 10.625$ (10) Å and $c = 12.955$ (15) Å; $\alpha = \beta = 90°$ and $\gamma = 120°$. Steric crowding (mostly F against F) limits the molecular symmetry to C_3, with no plane of symmetry and nine different F atom situations in each of the three equivalent $(CF_3)_3P$ groups. Small barriers to Fe–P and P–C bond rotation are indicated. For P-1, P-2, and P-3, ^{13}CO NMR spectra confirm the formulas, while $^{13}CF_3$ and ^{19}F spectra tend to be broad and poorly resolved. A sharp infrared peak at 2080 cm^{-1} is assigned to the 2,3-isomer in P-2 vapor, but the P-1 infrared spectrum is less decisive. The question of steric inhibition of isomerization in P-1 or P-2 is considered but not decided.

Introduction

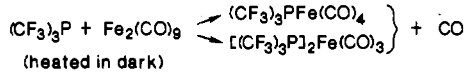
Phosphine substitution derivatives of iron pentacarbonyl have been reviewed with some emphasis upon isomerism.[1] Ligands such as PF_3 can occupy either axial (1 or 5) or equatorial (2, 3, or 4) vertices of the trigonal bipyramid. Some isomers have been distinguished by their C–O stretching frequencies, but equilibration through vibrational variation of bond angles was too fast (even at −110 °C) for such identification by NMR spectra. It was suggested that heavier phosphines might lead to slower isomerization, but no such effect had been observed. The present study of $(CF_3)_3P$ derivatives began with the idea that the size and shape of this ligand might inhibit their isomerization. Hints of such an effect were found, but truly conclusive evidence cannot be claimed.

Chemical Processes

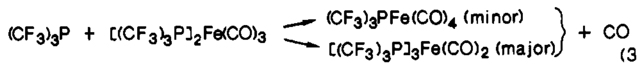
Displays 1–6 summarize the chemistry involved in the synthesis and further study of the $(CF_3)_3P$–Fe–CO complexes here designated as P-1, P-2, and P-3. All reactions except (2) occurred at ambient temperatures but required strong illumination, such as sunlight.



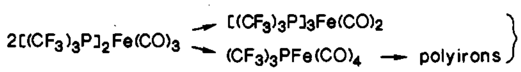
$$(CF_3)_3P + Fe(CO)_5 \rightarrow \left.\begin{matrix} (CF_3)_3PFe(CO)_4 \\ [(CF_3)_3P]_2Fe(CO)_3 \\ Fe_2(CO)_9 \text{ (major)} \end{matrix}\right\} + CO \quad (1)$$



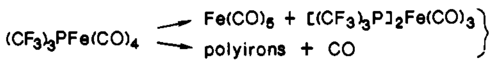
$$\underset{\text{(heated in dark)}}{(CF_3)_3P + Fe_2(CO)_9} \rightarrow \left.\begin{matrix} (CF_3)_3PFe(CO)_4 \\ [(CF_3)_3P]_2Fe(CO)_3 \end{matrix}\right\} + CO \quad (2)$$



$$(CF_3)_3P + [(CF_3)_3P]_2Fe(CO)_3 \rightarrow \left.\begin{matrix} (CF_3)_3PFe(CO)_4 \text{ (minor)} \\ [(CF_3)_3P]_3Fe(CO)_2 \text{ (major)} \end{matrix}\right\} + CO \quad (3)$$



$$2[(CF_3)_3P]_2Fe(CO)_3 \rightarrow \left.\begin{matrix} [(CF_3)_3P]_3Fe(CO)_2 \\ (CF_3)_3PFe(CO)_4 \rightarrow \text{polyirons} \end{matrix}\right\} \quad (4)$$



$$(CF_3)_3PFe(CO)_4 \rightarrow \left.\begin{matrix} Fe(CO)_5 + [(CF_3)_3P]_2Fe(CO)_3 \\ \text{polyirons} + CO \end{matrix}\right\} \quad (5)$$

$$[(CF_3)_3P]_2Fe(CO)_3 + PF_3 \rightleftharpoons (CF_3)_3P + CO + \text{expected complexes} \quad (6)$$

Here "polyirons" refers to at least three kinds of $(CF_3)_3P$–Fe_n–CO complexes: brown, green, and acetone insoluble. It is assumed that they are formed directly from P-1, or less probably by loss of $(CF_3)_3P$ from P-2. Polyirons with more than one $(CF_3)_3P$ on the same Fe atom would be sterically crowded. For this reason, P-3 could form polyirons only by loss of more than one $(CF_3)_3P$, requiring energy extremes possibly sufficient to destroy this ligand.

It is clear that display 3 includes the disproportionation process (4), but the excess $(CF_3)_3P$ suppressed P-1 so well that the secondary formation of polyirons could be neglected when the stoichiometry was used to prove molecular formulas.

The formula $(CF_3)_3PFe(CO)_4$ for P-1 was proved by the quantitative displacement of CO and $(CF_3)_3P$ by action of iodine. A larger molecule would not be consistent with its volatility. For P-2 the iodine reaction could not be completed, and P-3 failed to react with iodine. However, only the formulas $[(CF_3)_3P]_2Fe(CO)_3$ for P-2 and $[(CF_3)_3P]_3Fe(CO)_2$ for P-3 agreed with the quantitative results of process 3; and then the X-ray crystallography proving the formula of P-3 left no doubt of P-2.

The purpose of process 6 was to explore the ligand strength of PF_3 relative to $(CF_3)_3P$ and CO. There was no full analysis of the resulting complicated mixture, but there was no doubt that the most volatile fraction was rich in $Fe(CO)_4PF_3$; and less volatile material surely retained $(CF_3)_3P$ and CO. Nonvolatile polyirons also were evident. The further pursuit of this three-ligand system must be assigned to the future.

Structural Discussion

Isomerism and Steric Compression. The geometric relations in each of the three new molecules $(CF_3)_3PFe(CO)_4$ ("P-1"), $[(CF_3)_3P]_2Fe(CO)_3$ ("P-2"), and $[(CF_3)_3P]_3Fe(CO)_2$ ("P-3") can be examined by means of soldered wire models in which the outer atoms are represented by terminal points from which their van der Waals radii may be extended. It is immediately apparent that no two $(CF_3)_3P$ units can be placed only 90° apart: P-2 must be limited to the 1,5- and 2,3-isomers and only equatorial placement of these ligands can occur in P-3. No P-4 should be possible, nor can any $Fe_2(CO)_9$ derivative have more than one $(CF_3)_3P$ on each iron atom. In fact, substitution ceases abruptly at P-3, and the conversion of P-2 to P-3 is not complicated by formation of polyiron products—which indeed are involved in the conversion of P-1 to P-2.

In axial P-1, each CF_3 group might fit one F into a notch between two equatorial O atoms, but then there would be three strong F–F compressions, requiring various distortions and barriers to P–CF_3 bond rotation. Some relief could be found by pushing the equatorial O atoms out of the equatorial plane.

In equatorial P-1, only the axial CO units would be sterically important, but they surely would not fit into three CF_3 units without conflict.

The infrared spectra of P-1 are not decisive; one reason for broad and unresolved absorption may be the variable effects of steric compression.

In axial P-2, each $(CF_3)_3P$ group would encounter three O atoms at 90°, doubling the steric problem found in axial P-1 and allowing no relief by retreat of the CO units. In equatorial P-2, the P–Fe–P bond angle must be at least 120°, and there is not much resistance to retreat of the two axial CO units from compression by F atoms. This situation may be fairly comfortable in view of the closer ligand–ligand contact in the stable complex $[(CF_3)_3P]_2Ni(CO)_2$,[2] but the distorted structure of equatorial P-3

---

[1] Clark, R. J.; Busch, M. A. *Acc. Chem. Res.* **1973**, *6*, 249.

0020-1669/86/1325-4751$01.50/0

(see X-ray study) suggests what may be expected also for equatorial P-2, shown by its infrared spectrum to be at least strongly predominant or even exclusive. The solid might have either structure: as the crystals form from the glass at low temperatures, the isomer favored by crystal packing might prevail.

In P-3 the crowded 27 F atoms and 2 O atoms shield the central Fe atom from attack by air; and like the similarly shielded Ni atom in $[(CF_3)_2PF]_4Ni$,[3] this Fe strongly resists attack by iodine for analytical purposes.

The Question of Slow Isomerization. The possibility of slow interconversion of P-1 or P-2 isomers may be considered because the fitting of atoms into notches between neighbor atoms implies energy barriers which must be overcome simultaneously during such an isomerization. A final theoretical treatment of this subject would require calculations at the van der Waals level of uncertainty. Moreover, if one isomer is decidedly favored, the observation of such a conversion may be remarkably difficult. The following observations, mostly concerning P-1, may be relevant.

The initial P-1 samples, coming from sunlight, were liquids at 25 °C. Crystals (mp 45 °C) appeared only after the final traces of impurities had been removed by high-vacuum fractional condensation in subdued light. Exposed again to sunlight, the crystals melted instantaneously—before decomposition products could have lowered the melting range by more than 20 °C. The energy of sunlight could support at least a moderate population of the less stable isomer, which would isomerize in the dark.

Stored in the dark, pure P-1 crystals develop a glassy component. In a container which has been sealed off in vacuo, clean crystals are reformed by sublimation in situ. A small population of the less stable isomer, forming on the surface of each crystal, would be consistent with this observation.

The ^{31}P NMR spectrum of each P-1 sample showed the same set of interlaced peaks at 2% intensity, indicating at least one multiplet having the same J_{PCF} value (86 s^{-1}) as the main pattern. Neither P-2 nor P-3 would appear in that region. Polyiron complexes could not have been present. However, the multiplicity of this 2% component could not be determined, and there were other small peaks above the noise level.

In sum, then, the facts suggest slow interconversion of the P-1 isomers, but new information would be needed for certainty.

The slow conversion of glassy P-2 to crystals below −23 °C would not necessarily involve isomerization.

Experimental Methods

Volatile substances were managed by high-vacuum methods,[4] including use of mercury float valves having extended U-regions; they served both as grease-free, leak-proof seals and as short-range manometers. For quantitative transfer of such a slightly volatile compound as P-2, absorption by grease must be avoided: weighing bulbs were closed by O-ring valves.

For the best photochemical experiments the container was a 100-mL bulb with 0.7-mm wall thickness. Its shape was mainly cylindrical, with a conical bottom. It was closed by a straight-bore stopcock, making it possible to insert the long stem of a drawn-capillary pipette for bringing in a solvent and removing solutions of nonvolatile products. For high-vacuum sublimation of P-3 (conveniently at 70 °C) such a solution was brought into a tube connected through a standard-taper joint (made fast by Apiezon wax W) to a weighable U-tube having a straight-bore stopcock leading through a standard-taper joint to the vacuum line. Loss through this U-tube was avoided by cooling to 0 °C.

Carbon monoxide was collected by an automatic Sprengel pump[5] and measured over mercury. The free ligand $(CF_3)_3P$ passed a high-vacuum U-trap at −90 °C and was identified by its 2.2 mm volatility at −78.5 °C. Similarly, $Fe(CO)_5$ could be removed by repeated distillations through a U-trap at −30 °C. Quantitative isolation of P-1 and P-2 could be done only in subdued daylight from a north window; fluorescent lighting might cause decomposition as fast as the impurities were removed. P-1 was delivered through a U-trap at 0 °C, repeatedly until the P-2 condensate was pure; then the P-1 was passed through a U-trap at −10 °C, any condensate in which was reprocessed.

Residues not volatile at 70 °C could be determined by weighing the reaction bulb before and after cleaning. Their acetone solutions often had the color of Fe_3 carbonyls.

The Monophosphine Complex $(CF_3)_3PFe(CO)_4$ (P-1)

Synthesis. The best way to make P-1, with P-2 as an unavoidable byproduct, begins with photochemical action by $(CF_3)_3P$ on $Fe(CO)_5$. The purely thermal reaction is too slow at 100 °C, at which irreversible decomposition occurs. In the most accurate quantitative experiment, 1.33 mmol of $(CF_3)_3P$ and 1.21 mmol of $Fe(CO)_5$ were exposed to bright sunlight, quickly depositing on the bulb wall a yellow solid which limited the access of light. After 70 min, the liberated CO amounted to 0.74 mmol, with consumption of 1.05 mmol of $Fe(CO)_5$, but only 0.268 mmol of $(CF_3)_3P$ had been consumed. The yield of P-1 now was 0.180 mmol, with 0.024 mmol of P-2. Thus the empirical formula of the yellow solid was calculated to be $Fe(CO)_{4.4}[(CF_3)_3P]_{0.15}$—almost exclusively $Fe_2(CO)_9$.

This nonvolatile product, with the unused $Fe(CO)_5$ and $(CF_3)_3P$, was heated for 50 min at 75–81 °C (dark, in an oven), bringing the total evolution of CO to 0.970 mmol and the consumed $(CF_3)_3P$ to 0.915 mmol. The final yield of P-1 was 0.592 mmol and of P-2 was 0.122 mmol, together representing 96% of the consumed $Fe(CO)_5$ and 91% of the consumed $(CF_3)_3P$. The final black residue weighed 23 mg. P-3 was not observed.

A less efficient but more extensive experiment is chemically interesting. The quantitative data could be interpreted most simply by eq 7–9 with millimole quantities. However, most probably the Fe_2 and Fe_3 complexes included $(CF_3)_3P$.

$$\underset{3.31}{\mathrm{Fe(CO)_5}} + \underset{\substack{4.41\\-2.30\\2.11}}{\mathrm{(CF_3)_3P}} \rightarrow \underset{3.11}{\mathrm{CO}} + \underset{0.21}{\mathrm{Fe_2(CO)_9}} + \underset{0.111}{\mathrm{Fe_3(CO)_{12}}} + \text{volatiles} \tag{7}$$

$$\underset{0.21}{\mathrm{Fe_2(CO)_9}} + \underset{0.43}{\mathrm{2(CF_3)_3P}} \rightarrow \underset{0.21}{\mathrm{CO}} + \underset{0.43}{\mathrm{2(CF_3)_3PFe(CO)_4}} \tag{8}$$

$$\underset{0.111}{\mathrm{Fe_3(CO)_{12}}} + \underset{0.33}{\mathrm{3(CF_3)_3P}} \rightarrow \underset{0.33}{\mathrm{3(CF_3)_3PFe(CO)_4}} \tag{9}$$

The initial processes here occurred during 320 min in bright sunlight, with rotation of the bulb. Then the bulb was heated for 30 min at 100 °C in normal daylight. The final recovery of $(CF_3)_3P$ was 1.34 mmol; consumed, 3.07 mmol. The final yield of P-1 was 2.068 mmol and of P-2, 0.38 mmol, together representing 74% of the (wholly consumed) $Fe(CO)_5$ and 96% of the consumed $(CF_3)_3P$. Thus the rough empirical formula of the final black residue would be $(CF_3)_3PFe_{3.8}(CO)_{11}$, including unconverted Fe_2 and Fe_3 complexes, and some P-3 which was not isolated.

Analysis. A slightly glassy sample of highly purified P-1 was treated with iodine, requiring 1 h for 97% displacement of CO and $(CF_3)_3P$. After 2 h, the 0.411-mmol sample had given 1.602 mmol of CO (99.0%) and 0.410 mmol of $(CF_3)_3P$ (99.8%). From this result, it is doubtful that the glassy character was due to impurities.

Characterization. The deeply yellow P-1 crystals (fresh from high-vacuum sublimation) melted sharply at 45 °C. P-1 usually appears first as a light brown liquid which solidifies late in the course of purification. The ^{13}C, ^{31}P, and ^{19}F NMR spectra of the "neat" liquid differed scarcely at all from those of a solution of the pure crystals. Thus it appears that some special hypothesis is required to explain why very small impurities cause liquefaction.

Photolysis. Although pure P-1 is stable for weeks in the dark (or at least 16 h at 80 °C), it responds fairly promptly to fluorescent lighting. A 0.581-mmol sample, occupying a bulb-wall surface of approximately 70 cm^2 and exposed for 60 min at 24 °C, was extensively melted, but only 0.0045 mmol of $(CF_3)_3P$ and 0.009 mmol of $Fe(CO)_5$ were liberated. A trace of P-2 also was seen, and nonvolatile black material also was slight. The remaining P-1, now under ice–acetone at −12 °C, was similarly exposed for 85 min, yielding 0.014 mmol of $Fe(CO)_5$. Even such small impurities seem strongly to lower the melting point, but a metastable

---

(2) Emeléus, H. J.; Smith, J. D. *J. Chem. Soc.* **1958**, 527.

(3) Burg, A. B.; Street, G. B. *Inorg. Chem.* **1966**, *5*, 1535.

(4) Methods much as described by Stock, A. *Hydrides of Boron and Silicon*; Cornell University Press: Ithaca, NY, 1933, Chapter 30, but with numerous modifications and new devices based upon more extensive experience.

(5) Burg, A. B. *Inorg. Chem.* **1983**, *22*, 2573—ref 6.

isomer could have the same effect.

Direct sunlight proved to be far more destructive. In the most accurate of a number of quantitative experiments, 1.05 mmol of P-1, again spread over a 70-cm^2 wall area in a 100-mL bulb, liquefied completely during a 4.0-min exposure; then 0.93 mmol of P-1 could be recovered. The consumed 0.12 mmol of P-1 had yielded 0.049 mmol of $Fe(CO)_5$, suggesting that 84% of it had disproportionated; cf. reaction 5. However, since the yield of P-2 was only 0.032 mmol, some of this may have been destroyed according to reaction 4. Indeed, a few very tiny crystals of P-3 could be sublimed out of the minute black residue under high vacuum. Also found was 0.018 mmol of $(CF_3)_3P$, indicating an upper limit for such processes as (10) and (11), which seem

$$2(CF_3)_3PFe(CO)_4 \rightarrow (CF_3)_3P + (CF_3)_3PFe_2(CO)_8 \quad (10)$$

$$3(CF_3)_3PFe(CO)_4 \rightarrow 3(CF_3)_3P + Fe_3(CO)_{12} \quad (11)$$

probable since no CO appeared. Indeed, the final black residue was green in acetone, suggesting Fe_3 complexes. In sum, the expected disproportionation was by far the major result, with minor processes complicating the stoichiometry.

The Bis(phosphine) Complex $[(CF_3)_3P]_2Fe(CO)_3$ (P-2)

Synthesis. Good samples of P-2 were obtained as byproducts of the P-1 synthesis. However, when P-2 was sought more directly by using a higher ratio of $(CF_3)_3P$ to $Fe(CO)_5$, with adequate sunlight, there was major formation of polyiron material and P-3. It is important to remove the P-2 frequently, with small additions of $(CF_3)_3P$.

A tedious but fairly satisfactory P-2 synthesis began with 5.33 mmol of $Fe(CO)_5$ and 4.75 mmol of $(CF_3)_3P$, of which three further portions were added during an 11-step process in which the nonvolatiles were heated with the remaining $(CF_3)_3P$ four times at 90 °C to convert the Fe_2 complexes. At this point, 4.70 mmol of $Fe(CO)_5$ and 5.91 mmol of $(CF_3)_3P$ had been consumed, with liberation of 6.10 mmol of CO. The yield of P-1 now was 2.72 mmol (57%) and of P-2, 1.33 mmol (28%). With the P-2 removed and addition of $(CF_3)_3P$ in steps to a total of 12.24 mmol, the process went forward for nine more steps, consuming all of the $Fe(CO)_5$ and eliminating all but 0.29 mmol of the P-1 (5.4% yield). The total free CO now was 11.75 mmol and the consumed $(CF_3)_3P$ 10.70 mmol. The final yield of P-2 was 2.43 mmol (45%), at considerable cost of total efficiency. The nonvolatile residue would be formulated empirically as $Fe(CO)_{2.52}[(CF_3)_3P]_{2.13}$—very close to an Fe_2L_9 type. However, it was from this residue that the first small samples of P-3 were sublimed out in vacuo at 70 °C.

Characterization. The volatility of P-2 is close to 0.4 mm at 25 °C. The −23 °C melting point (after crystallization from the glass) appears to be repeatable. Analysis by iodine (excess at 90 °C; 150 min) failed because the reaction was only 70% complete. However, the formula of P-2 is not in doubt in view of the quantitative stoichiometry of its conversion to P-3 (with P-1 and minimum nonvolatiles) and the NMR triplet coupling of ^{13}C to ^{31}P, proving two P atoms per molecule.

Decomposition and Photolysis. Vividly yellow P-2 (0.246 mmol) was not darkened during 21 h in a 10-mL tube at 58 °C, but 2% decomposition was indicated by recovery of 0.0007 mmol of $(CF_3)_3P$ and 0.0017 mmol of P-1. After some days in diffuse daylight, an NMR sample (in $DCCl_3$) had a ^{31}P spectrum showing traces of P-3 and $(CF_3)_3P$, with a definite increase in the sharp decad for the P-1 impurity; slight disproportionation and dissociation were indicated, but CO and $Fe(CO)_5$ were not found.

In bright sunlight, a 0.333-mmol sample, exposed for 9 min (area, 30 cm^2), yielded 0.0107 mmol of $(CF_3)_3P$, 0.0023 mmol of $Fe(CO)_2$, and 0.035 mmol of P-1, with recovery of 0.246 mmol (74%) of the P-2. There was no trace of CO. From the 38-mg residue, 10 mg (0.012 mmol) of P-3 could be pumped off. The remainder now weighed 28 mg (calculated 25 mg) with an empirical formula near $Fe[(CF_3)_3P]_{2.45}(CO)_{0.2}$. Part of this was green in acetone, but the rest could not be dissolved in nitric acid.

In sum, then, this photolysis was like that of P-1: both dissociation and disproportionation were evident.

Photolysis with Trifluorophosphine. An exploratory experiment employed 0.354 mmol of P-2 with 3.50 mmol of PF_3, in a 90-mL bulb exposed to bright sunlight for 2 h, liberating 0.540 mmol of CO and 0.517 mmol of $(CF_3)_3P$ but consuming only 0.799 mmol of PF_3. Thus the simple ligand displacement was complicated by the formation of polyiron material, appearing as a tan nonvolatile product. The stoichiometry indicated that this was unexpectedly rich in $(CF_3)_3P$ and poor in CO and PF_3. It might include ligand-deficient $(CF_3)_3P$–Fe–L complexes in which steric effects prevent achievement of an 18-electron shell.

The main volatile substitution product here was a 0.163-mmol fraction having volatility 11 mm at 0 °C and molecular weight near 250, consistent with $Fe(CO)_4PF_3$. Also found were a 0.027-mmol fraction about as volatile as P-1 and having molecular weight near 500—understood as $(CF_3)_3PFe(CO)_n(PF_3)_{4-n}$—and a 22-mg fraction about as volatile as P-2, presumed to be a mixture of the type $[(CF_3)_3P]_2Fe(CO)_m(PF_3)_{3-m}$. It is noted that replacement of CO by PF_3 only slightly affects volatility.[6] The presence of $Fe(CO)_4PF_3$ here would imply that the synthesis of P-2 is reversible.

A fuller study of this complicated three-ligand system is beyond the present purpose.

The Tris(phosphine) Complex $[(CF_3)_3P]_3Fe(CO)_2$ (P-3)

Monitored Synthesis. A 0.720-mmol sample of P-2 with 0.932 mmol of $(CF_3)_3P$ was exposed to bright sunlight for 2 h, consuming 0.676 mmol of the P-2 and 0.494 mmol of the $(CF_3)_3P$ and releasing 0.528 mmol of CO. Reaction 4 accounted for the observation of 0.058 mmol of P-1; then the empirical formula of the main solid product was $[(CF_3)_3P]_{2.94}Fe(CO)_{2.08}$, including a slight black residue (soluble in chloroform) left after the orange crystals had been sublimed off. This residue would be polyiron material, allowance for which would make the P-3 empirical formula more accurate.

Physical Properties. Pure P-3 melts sharply (under dry nitrogen) at 90 °C. The immediate product of the synthesis appeared as pastel-tan fernlike fronds, resubliming fairly promptly to more compact, strongly orange lumps. Very slow sublimation through the high-vacuum line at 25 °C is possible, but not convenient.

P-3 is slightly soluble in benzene or dichloromethane, but insoluble in water or acetone; indeed, acetone could be used to extract impurities from it. Its solubility in $DCCl_3$ was roughly estimated as 20 mg per mL—enough to permit the use of $DCCl_3$ as a lock solvent for some NMR spectra, barely including $^{13}CF_3$. For ^{13}CO and ^{31}P, n-C_6F_{14} is far better: in it, P-3 is about 15% soluble at 25 °C, but at 0 °C the solubility is closer to 2%, so that temperature effects for ^{31}P could not be studied effectively.

Infrared Spectra

Only the strongest and structurally most significant infrared bands for P-1, P-2, and P-3 were recorded, all at 25 °C, by means of the Perkin-Elmer 281 instrument. The frequencies (cm^{-1}) are shown in Table I, with relative intensities in parentheses.

The Structure Problem of P-1. The C–O stretching bands for P-1 are shown in Figure 1. The resolution of the broad low-frequency band was not effectively improved by narrowing the slit to half-normal.

The main dilemma here concerns the meaning of the band near 2100 cm^{-1}. The closely analogous case of $PF_3Fe(CO)_4$ has been discussed mathematically by Haas and Sheline;[7] thus the relatively weak band in the higher frequency region may be assigned to the A_1 mode of either isomer, or both.

In the liquid or vapor phase, the equatorial P-1 isomer might predominate because the CF_3 groups can press strongly upon only two CO units rather than three, but for crystal packing, the more symmetrical (C_{3v}) axial isomer might be chosen, despite CF_3 pressure upon three equatorial CO units. If the very weak interlaced peaks in the ^{31}P NMR spectrum are assignable to an isomer, the meaning is a strong preference for the other isomer,

---

[6] Clark, R. J. *Inorg. Chem.* **1964**, *3*, 1397.

[7] Haas, H.; Sheline, R. K. *J. Chem. Phys.* **1969**, *47*, 2996.

Table I. Infrared Spectra (cm^{-1})[a]

P-1 (vapor)	P-2 (vapor)	P-3 (in $DCCl_3$)	P-3 (solid)
2097 (80)	2080 (75)		
2022 (300)	2025 (460)	2008 (40)	2014 (180)
1230 (100)	1225 (250)	1218 (50)	1217 (50)
1189 (80)	1188 (160)	1190 (50)	1182 (50)
		1180 sh (41)	
1156 (65)	1149 (154)	1157 (45)	1154 (45)
1134 (67)	1132 (116)	1124 (36)	1120 (40)
		906 (80)	900 (67)
740 (6)[b]	733 (98)	730 (68)[b]	725 (67)
638 (60)		643 (64)	?
618 (30)	620 (70)		

[a] The relative intensities in parentheses, for P-1 and P-2 vapors, are calculated as $k = (100/PL) \log (I_0/I)$ for gas pressure P and path length L, both in centimeters. For P-3, the arbitrary intensity scale is based upon 50 for the 1218 and 1217 peaks. [b] These are broad peaks, probably composite. For P-2, the sharp 733 peak has an indefinite lower frequency shoulder.

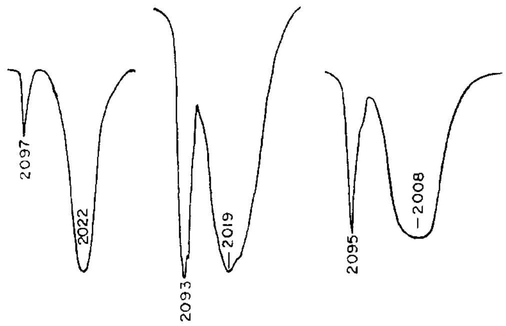


Figure 1. The C–O stretching bands of P-1 vapor (left), solid (right), and (middle) for the chloroform solution. These are tracings, with the noise averaged out. With the slit program at half of the normal width, the solution spectrum showed a hint of band superpositions.

but this is very uncertain evidence. Even an X-ray study of the crystals would not surely solve the problem of structure in the liquid or vapor phase, wherein the predominance of one isomer is not certain.

Equatorial P-2. The unique equatorial C–O stretching mode in equatorial P-2 accounts for the strong and relatively sharp 2080 cm^{-1} band, not expected for the axial isomer. The C–O stretching at 2025 cm^{-1} (presumably B_1) also is sharp, arguing against a mixture including the axial isomer. The sharpness here would suggest also that the axial O atoms are not seriously disturbed by variability of impingement by F atoms.

P-3 Results. The single sharp peak for either solid or dissolved P-3 in the C–O stretching region is consistent with the only sterically possible structure, having three equatorial $(CF_3)_3P$ ligands. The C–F stretching bands in the 1120–1230 cm^{-1} region show a pattern of relative intensities and frequencies very similar to that of the free ligand $(CF_3)_3P$, but with the frequencies slightly lower for this solid compound P-3. It appears that C-F stretching is not much affected by attachment of $(CF_3)_3P$ to iron.

The 600–740 cm^{-1} range would include C–O bending, CF_3 deformation, and Fe–C stretching, often superposed. Structural assignments here would be difficult for all three compounds.

NMR Spectra

The NMR results for P-1, P-2, and P-3 (Table II) were recorded mostly by the IBM WP27OSY-FT instrument, but two important spectra came from the Varian XL 200-FT instrument, operated by Dr. Surya Prakash in our Loker Hydrocarbon Institute. As before,[8] the chemical shifts δ are positive upfield from Cl_3CF, negative downfield from H_3PO_4, and positive downfield from $(CH_3)_4Si$ (for ^{13}C). Symbols like $_nJ_{XYZ}$, in s^{-1} ("Hz"), show multiplicity n for coupling of the observed nucleus X to nucleus Z. The solvent usually was $DCCl_3$, but when C_6F_{14} was used for P-3 in a 5-mm tube surrounded by acetone-d_6 in a 10-mm tube, the ^{31}P spectrum appeared 1.1 ppm closer to H_3PO_4, even after correction for different geometry and lock material.

Table II. NMR Data [δ and J (s^{-1})]

	$(CF_3)_3PFe(CO)_4$	$[(CF_3)_3P]_2Fe(CO)_3$	$[(CF_3)_3P]_3Fe(CO)_2$
δ_{CO}	210.3	209.4	210.0
J_{CP}[a]	2.9	13.9	31.5
δ_{CF}	124.4	123.7	123.6
$_4J_{CF}$	320	322	324
$_2J_{CP}$	60.3	66	66
$_7J_{CPCF}$	3.2		
δ_P	−89.8	−95.3	−96.4
$_{10}J_{PCF}$	86.9	86.4	86.4
δ_F	57.5	56.3	54.6
$_2J_{FCP}$	86.1	86.5	86.1[b]

[a] Respective multiplicities 2, 3, and 4. For all other J's, multiplicity (needed for interpretation) is indicated by the lower left subscripts. It is suggested that this direct and simple way to indicate coupling multiplicity might well be more widely adopted; cf. *Inorg. Chem.* **1981**, *20*, 2740. [b] The main peaks here carry inward shoulders (72 s^{-1} apart), between which there is a low-hanging catenary; complexity is evident.

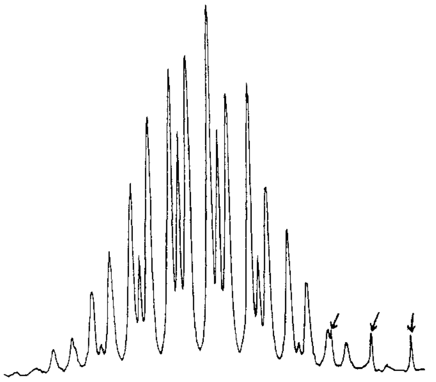


Figure 2. The ^{31}P NMR spectrum of P-2 (saturated solution in $DCCl_3$), recorded by the XL200-FT instrument. The pattern from the WP27OSY-FT instrument is the same except for the relative heights of the major peaks and slight differences of spacing. The sharp upfield peaks marked with arrows belong to the P-1 impurity, which does not interfere. With the 270 instrument, the peak spacings are nearly the same: $_{10}J_{PCF} = 86.4$ s^{-1} and $_2J = 49$ s^{-1} for the major multiplets. There is also a multiplet of minor peaks ($J = 87.3$ s^{-1}), neatly bisecting alternating regions between the larger peaks.

The half-height widths (hereinafter, "hw", in s^{-1}) of some peaks seem worthy of discussion. In P-1, ^{13}CO had an hw of 2.5, while the $Fe(CO)_5$ impurity showed an hw of 1.4; possibly the three equatorial CO and one axial CO do not rapidly average out in P-1 as they do in $Fe(CO)_5$, but their δ values cannot be very different. Hence the very clean and sharp triplet for ^{13}CO in P-2 (hw = 2.1) does not provide an argument for the 1,5-(axial P) isomer, for here the infrared spectrum indicates the 2,3-isomer, at least in the vapor phase. For P-3, the XL200-FT instrument gave hw = 4, with different instrumental conditions.

A more dramatic contrast is found in the $^{13}CF_3$ spectra: for P-1 hw = 1.8, with $_7J_{CPCF}$ well resolved, but for P-2 and P-3 hw = 19 ± 4, chiefly because J_{CPCF} is not resolved for either. This failure of resolution may be attributed to complex relationships between or within $(CF_3)_3P$ groups, correlating with the remarkable complexity of the ^{31}P spectra (Figures 2 and 3).

For P-3 the ^{19}F spectrum has complexity like that shown by $(CF_3PCF_2)_3$, wherein the two equatorial CF_3 groups are compressed against a CF_2 connecting group.[9] For ^{13}CO in P-3, hw = 4; for $^{13}CF_3$, hw = 11.

The ^{31}P spectrum of P-1 is an apparently simple decad, with no complication except the interlaced multiplet with about 2% relative intensity, cf. P-1 characterization. Far more complex are P-2 and P-3 (Figures 2 and 3). For P-2, five different records

---

(8) Burg, A. B. *Inorg. Chem.* **1985**, *24*, 3342 et ante.

(9) Burg, A. B. *Inorg. Chem.* **1983**, *22*, 2577—Figure 2.

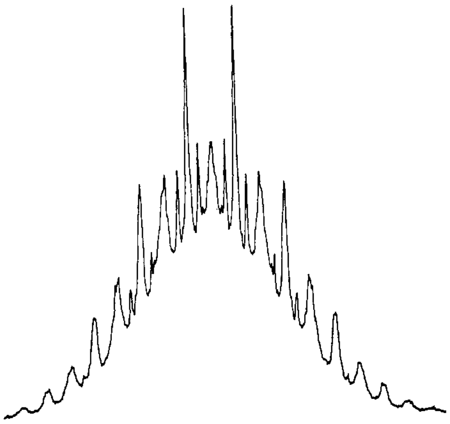


Figure 3. The ^{31}P NMR spectrum of P-3 (saturated solution in C_6F_{14}; WP27OSY-FT instrument). The pattern of sharp peaks looks like a decad of 1:2:1 triplets with $_{10}J_{PCF} = 86.4$ and $_3J = 24$ s^{-1}, but this $_3J$ probably is illusory. The broadening of the outer members suggests that there are two such decads, concentrically superposed but with $_{10}J_{PCF}$ differing by about 2 s^{-1}. The tip of the broad central peak is bifurcated, with separation 2.6 s^{-1}. The tiny peaks symmetrically surrounding this central peak seem to be members of another multiplet with J near 34 s^{-1}.

Table III. Summary of P-3 X-ray Crystallography

formula	$[(CF_3)_3P]_3Fe(CO)_2$
mol wt	825.85
cryst size, mm	0.50 × 0.40 × 0.30
cryst formatn	from vapor during synthesis
instrument	Nicolet/Syntex $P2_1$
radiatn	Mo $K\alpha$ (0.71069 Å)
2θ limit	45°
temp	25 °C
method of structure soln	standard heavy atoms
total reflctns for refinemen.	2131 [428 with $I > 3\sigma(I)$]
refinement program	SHELX-76
agreement factors	$R = 0.065$; $R_w = 0.058$
space group	$P6_3$ (No. 173)
unit cell[a]	$a = b = 10.625$ (10) Å
	$c = 12.955$ (15) Å
	$\alpha = \beta = 90°$; $\gamma = 120°$
	$V = 1267$ (2) $Å^3$
	$Z = 2$
D(calcd)	1.09 g/cm^3

[a] Estimated standard deviations in parentheses.

of the ^{31}P spectrum showed peaks symmetrically placed, but with inconsistent peak heights. In principle, these P-2 and P-3 spectra might be compared with those of various double-P spectra on file in this laboratory. For $R(CF_3)PCF_2P(CF_3)CHF_2$ (R = Cl or CH_3) resolution is almost absent. The spectra of $P_2(CF_3)_4$ and $(CF_3)_2POP(CF_3)_2$ are somehwat similar to Figures 2 and 3, but with sharp peaks fully resolved. P-2 and P-3 show curious alternations of sharp and broad peaks suggestive of unresolved complexity. This effect is more pronounced for P-3.

X-ray Crystallography of P-3

An X-ray analysis was performed by Dr. Robert Bau and Ms. Kuei-Shang Huang, on a single block-shaped crystal of $[(CF_3)_3P]_3Fe(CO)_2$ taken directly from the wall of the container in which it was photochemically formed from P-2 and $(CF_3)_3P$. The nontwinned crystal was selected with the aid of a polarizing microscope and enclosed in a thin-walled quartz capillary tube.

The conditions and numerical results of this X-ray study are listed in Tables III and IV. The equatorial placement of the three P atoms on the trigonal bipyramid is beyond doubt, but the analysis showed large motions of the F atoms: it appears that the energy wells for vibration (including bond rotation) are broad and shallow.

Table IV. Average Bond Parameters[a] for P-3

	Bond Lengths (Å)		
Fe–C	1.740 (21)	C–F	1.300 (10)
Fe–P	2.151 (4)	P–C	1.820 (22)
C–O	1.201 (20)		
	Bond Angles (deg)		
C–Fe–P	90.0 (4)	F–C–F	108.7 (13)
Fe–P–C	121.1 (5)	C–P–C	95.8 (6)
P–C–F	110.1 (16)	O–C–Fe	180.0 (0)

[a] Estimated standard deviations in parentheses.

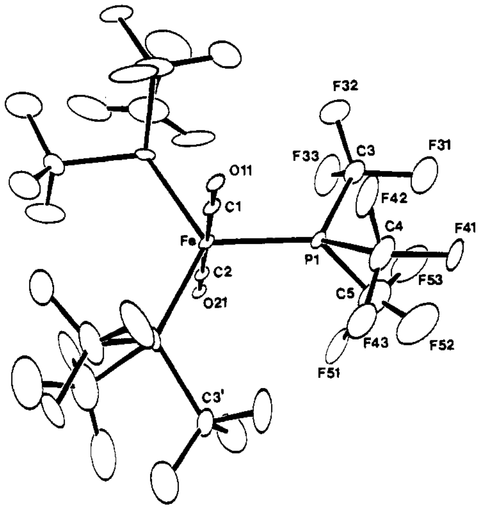


Figure 4. A perspective view of the P-3 molecule. The systematic numbering of atoms in one $(CF_3)_3P$ unit is repeated with each 120° rotation about the polar axis. It must be emphasized that this arrangement of atoms may not be the only way for the F atoms to minimize mutual contact; other patterns may occur in the liquid or vapor phase or in the fern-like crystals which could not be studied.

The P-3 molecule, shown as a bird's-eye view in Figure 4, is situated on a crystallographic rotational axis identical with the O–C–Fe–C–O axis of a trigonal bipyramid. The F atoms show a skew pattern as they repel O atoms or each other. As one views the picture from an infinite distance down the polar axis, the atoms C4 and C5 are eclipsed, with their six F atoms (41, 42, 43, 51, 52, and 53) forming a pattern distorted from the symmetry of C_2F_6. The third CF_3 group in the same $(CF_3)_3P$ unit has C3 and F31 at average positions within 0.003 Å of the FeP_3 (equatorial) plane; thus the F32–C3–F33 and C4–P1–C5 bond angles are bisected by that plane. However, the P1–C3 bond rotation may be almost free. Then also, the obvious incongruities in the sizes of the probability ellipsoids could not be reduced by variations in the calculational postulates. Nevertheless, some of the nine different F positions may be maintained well enough to explain the complexity of the ^{31}P and ^{19}F NMR spectra and the failure to resolve J_{CPCF} in the $^{13}CF_3$ spectrum.

Since the symmetry is only C_3, with no mirror plane, each crystal must be optically active. Each batch of crystals would deviate from enantiomeric equality by coin-flip statistics.

It is to be emphasized that different crystals may show slightly different arrangements of F atoms, allowing different ways for close neighbors to minimize repulsion. The present results are for only one block-shaped crystal; the fernlike crystals from the same synthesis would be far more difficult to mount for X-ray study. At low temperatures there might be a preference for a single structural type, and less thermal vibration might lead to more consistent X-ray results.

Acknowledgment. Thanks are due to Dr. Surya Prakash for NMR spectra on the Varian XL200-FT instrument, to Dr. K. L. Servis for good advice, and to Alan Kershaw for aid in the use of the IBM WP27OSY-FT instrument, acquisition of which was aided by the National Science Foundation. I am grateful also to Dr. Robert Bau and Ms. Kuei-Shang Huang for their determination of the crystal structure of P-3.

Supplementary Material Available: A table of final atomic parameters for $[(CF_3)_3P]_3Fe(CO)_2$ (1 page); a listing of calculated and observed structure factors for $[(CF_3)_3P]_3Fe(CO)_2$ (2 pages). Ordering information is given on any current masthead page.