for a given R group, the Pt nuclei are about equally shielded despite the charge difference and the change in sulfur coordination number. The similar δ ^{195}Pt ranges of these two types of compounds (ca. −3100 to −3200 ppm) are more deshielded than that of $[Pt(dien)(RSSR)]^{2+}$ complexes (ca. −3250 to −3320 ppm), which are in turn more deshielded than the range for $[Pt(dien)(RSR)]^{2+}$ complexes (ca. −3351 to −3375 ppm). The δ ^{195}Pt shielding order $RS^- < RSSR < RSR$ may reflect a decrease in the paramagnetic shielding term resulting from an increase in the ligand field splitting parameter ΔE.[30] A rationale for this order is not obvious, however. These data demonstrate that any of these classes of compounds can be identified in a mixture (provided the chemical shifts are not too near a boundary of the range for a given class). However, speciation of members within a class is not feasible owing to the width of the ^{195}Pt chemical shifts in these reagents, to which sulfur inversion[31-33] processes can also contribute in the case of $[Pt(dien)(SR_2)]^{2+}$, $[Pt(dien)(RSSR)]^{2+}$, and $\{[Pt(dien)]\}_2SR$ complexes.

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Cleavage of a Cyclotriphosphine Ring by Iron Carbonyls[1]

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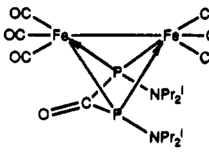
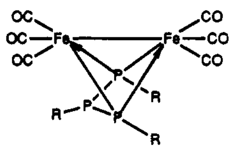
Reaction of tri-*tert*-butylcyclotriphosphine, t-Bu_3P_3, with $Fe(CO)_5$ in boiling toluene or with $Fe_3(CO)_{12}$ in boiling benzene gives yellow-brown crystalline t-$Bu_3P_3Fe_2(CO)_6$. An X-ray diffraction study of t-$Bu_3P_3Fe_2(CO)_6$ (orthorhombic, $P2_12_12_1$; a = 10.522 (5) Å, b = 12.188 (4) Å, c = 19.807 (8) Å, Z = 4) indicates an Fe–Fe bond (Fe–Fe = 2.602 (3) Å) and opening of the cyclotriphosphine P_3 triangle to give a P_3 chain (P1–P3 = 2.226 (6) Å, P2–P3 = 2.209 (6) Å) with an essentially nonbonding P1···P2 distance of 2.499 (6) Å between the end phosphorus atoms of this P_3 chain; the center atom of the P_3 chain is trivalent and not bonded directly to any iron atoms. Reaction of t-Bu_3P_3 with $Fe_2(CO)_9$ at room temperature gives not only this binuclear complex t-$Bu_3P_3Fe_2(CO)_6$ but also a trinuclear complex t-$Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$. X-ray diffraction of this trinuclear complex (monoclinic, $P2_1/n$; a = 9.180 (5) Å, b = 16.923 (7) Å, c = 19.186 (9) Å, β = 93.27 (4)°, Z = 4) indicates a structure similar to that of the binuclear complex t-$Bu_3P_3Fe_2(CO)_6$ but with an $Fe(CO)_4$ group bonded to the center phosphorus atom of the P_3 chain. Reaction of t-$Bu_3P_3Fe_2(CO)_6$ with hydrogen peroxide in ethanol and with sulfur in boiling toluene gives the corresponding oxide t-$Bu_3P_3OFe_2(CO)_6$ and sulfide t-$Bu_3P_3SFe_2(CO)_6$, respectively.

Introduction

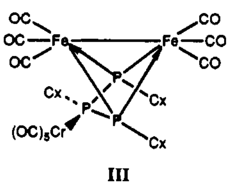
In recent years the reaction of $Na_2Fe(CO)_4$ with i-Pr_2NPCl_2 has been found to give as the major product the phosphorus-bridging carbonyl derivative $(i\text{-}Pr_2NP)_2COFe_2(CO)_6$ (I) in diethyl ether solution but the triphosphine derivative $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ (II; R = i-Pr_2N) in tetrahydrofuran solution.[2] The formation of II (R = i-Pr_2N) from the $Na_2Fe(CO)_4/i\text{-}Pr_2NPCl_2$ reaction is of interest because of the formation of a chain of three phosphorus atoms from the reductive coupling of three i-Pr_2NP units upon reaction of i-Pr_2NPCl_2 with the $Na_2Fe(CO)_4$. A related reductive coupling reaction occurs upon treatment of $(CxPCl_2)Fe(CO)_4$ (Cx = cyclohexyl) with $Na_2Cr_2(CO)_{10}$ to give the derivative $Cx_3P_3[Cr(CO)_5]Fe_2(CO)_6$ (III),[3] in which not only the outer phosphorus atoms of the triphosphine chain are bonded to iron atoms but also the central phosphorus atom of the triphosphine chain is coordinated to a $Cr(CO)_5$ group. This compound is closely related to the product $(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$ (IV) obtained by complexation of the central phosphorus atom in $(i\text{-}Pr_2NP)_2P(Cl)Fe_2(CO)_6$ (V) by reaction with $(thf)Cr(CO)_5$.[4] Other compounds containing a triphosphine hexacarbonyldiiron P_3Fe_2 unit have been obtained by the following methods:



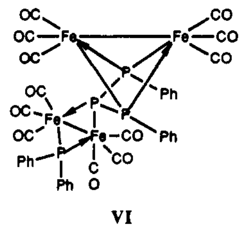
I



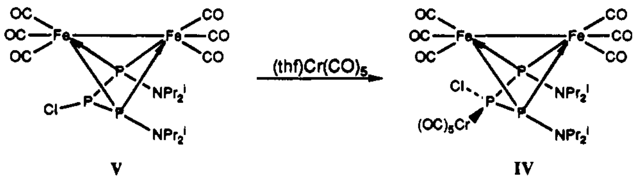
II



III



VI



V IV

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(1) Complexes of Trivalent Phosphorus Derivatives. 19. For part 18 of this series see King, R. B.; Cloyd, J. C., Jr.; Norins, M. E.; Reimann, R. H. *J. Coord. Chem.* **1977**, *7*, 23.

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Table I. ^{31}P NMR Spectra and Infrared $\nu(CO)$ Frequencies of Triphosphine Iron Carbonyl Derivatives

compound	^{31}P NMR, δ^a middle P	end P	$\lvert J(P–P)\rvert^b$	infrared $\nu(CO)$ frequencies,^{c} cm^{-1}
$(i\text{-}Pr_2NP)_3Fe_2(CO)_6$	292.2 t	170.3 d	264	2048 s, 2008 s, 1986 s, 1958 s, 1947 m
$t\text{-}Bu_3P_3Fe_2(CO)_6$	249.0 t	99.9 d	176	2050 s, 2012 s, 1982 s, 1971 s, 1960 s, 1932 w
$t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$	296.4 t	136.9 d	142	2063 m, 2045 s, 2016 s, 1988 s, 1967 s, 1956 s
$t\text{-}Bu_3P_3OFe_2(CO)_6$	170.2 t	179.4 d	184	2058 m, 2025 s, 1987 s, 1968 w
$t\text{-}Bu_3P_3SFe_2(CO)_6$	215.9 t	177.8 d	182	2056 s, 2023 s, 1987 s, 1967 s
$t\text{-}Bu_3P_3$	−109.6 t	−70.6 d	202	

[a] These ^{31}P NMR spectra were run in $CDCl_3$ solution: d = doublet; t = triplet. [b] These coupling constants are given in hertz. [c] These infrared $\nu(CO)$ frequencies were measured in hexane solution.

Table II. Proton and ^{13}C NMR Spectra of Triphosphine Iron Carbonyls

compound	proton NMR,^{a} δ	carbon-13 NMR,^{a,b} δ metal CO groups	quaternary C	methyl
$t\text{-}Bu_3P_3Fe_2(CO)_6$	1.43 d (11), 1.29 t (9)	213.3 d (12), 212.7 s	39.6 s, 30.6 s	30.4 s, 30.1 s
$t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$	1.60 s, 1.41 s	217.0 s, 213.1 s, 212.2 s	42.2 s, 30.1 s	32.2 s, 31.7 s
$t\text{-}Bu_3P_3OFe_2(CO)_6$	1.46 s	211.9 s	41.7 s	31.7 s, 27.9 s
$t\text{-}Bu_3P_3SFe_2(CO)_6$	1.62 d (17), 1.51 dd (10, 8)	212.3 d (6), 211.8 d (5)	51.0 s, 44.4 s	31.9 s, 29.6 s

[a] All of the proton NMR spectra were obtained in $CDCl_3$ solution: s = singlet, d = doublet, dd = double doublet, t = triplet. [b] All of the carbon-13 NMR spectra were obtained in $CDCl_3$ solution with added $Cr(acac)_3$.

(1) The triphenyltriphosphine derivative $Ph_3P_3Fe_2(CO)_6$ (II: R = phenyl) has been obtained by the following reaction sequence:[5]

$$(PhPH)_2Fe_2(CO)_6 + 2MeLi \rightarrow (PhPLi)_2Fe_2(CO)_6 + 2CH_4 \tag{1a}$$

$$(PhPLi)_2Fe_2(CO)_6 + PhPCl_2 \rightarrow Ph_3P_3Fe_2(CO)_6 + 2LiCl \tag{1b}$$

(2) Pyrolysis of the $\eta^1\eta^2$-diiron diphosphene complex $(PhP{=}PPh)Fe_2(CO)_6$ in boiling benzene gives a 70% yield of a yellow dimer of stoichiometry $Ph_4P_4Fe_4(CO)_{12}$ shown by X-ray diffraction to have structure VI, i.e., $Ph_2P_3[Fe_2(CO)_6(\mu_2\text{-}PPh_2)]Fe_2(CO)_6$ with a triphosphine chain and an "isolated" Ph_2P group formed by migration of a phenyl group from one phosphorus atom to another.[6]

Another possible approach to the synthesis of triphosphine hexacarbonyldiiron derivatives of the type $R_3P_3Fe_2(CO)_6$ uses the cleavage of a single phosphorus–phosphorus bond in a cyclotriphosphine ring with iron carbonyls. This paper reports the first example of a reaction of this type, namely cleavage of the P_3 ring in the readily available[7] tri-*tert*-butylcyclotriphosphine with iron carbonyls to give $t\text{-}Bu_3P_3Fe_2(CO)_6$ shown by X-ray diffraction to have the expected structure II (R = *tert*-butyl). In addition compounds are described in which the lone pair of the central phosphorus atom in $t\text{-}Bu_3P_3Fe_2(CO)_6$ has been complexed with an $Fe(CO)_4$ group or oxidized to the corresponding phosphine oxide or phosphine sulfide.

Experimental Section

Microanalyses were performed by the Atlantic Microanalytical Laboratory, Norcross (Atlanta), GA. Infrared spectra (Table I) were run in the 2200–1600 cm^{-1} metal–carbonyl region in hexane solution and recorded on a Perkin-Elmer Model 1600 Fourier transform infrared spectrometer calibrated against polystyrene film. Proton (Table II), carbon-13 (Table II), and phosphorus-31 (Table I) NMR spectra were run on a Bruker 300-MHz spectrometer with internal tetramethylsilane, internal tetramethylsilane, and external 85% phosphoric acid, respectively, as references. Carbon-13 and phosphorus-31 NMR spectra were normally run with proton decoupling. All chemical shifts (δ) are given downfield from the reference. The relaxation reagent $Cr(acac)_3$[8] was added to the carbon-13 NMR samples in order to obtain better spectra in the metal carbonyl region. Melting and decomposition points were taken in capillaries and are uncorrected.

Table III. Reactions of $t\text{-}Bu_3P_3$ with $Fe_2(CO)_9$ under Different Conditions^a

conditions	Fe_2/Fe_3 mole ratio^b
boiling hexane	7.7
toluene at room temperature	2.6
diethyl ether at room temperature	2.3
tetrahydrofuran at room temperature	6.5

[a] All of these reactions were carried out using a 2:1 mole ratio of $Fe_2(CO)_9$ to $t\text{-}Bu_3P_3$. [b] This refers to the $t\text{-}Bu_3P_3Fe_2(CO)_6/t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$ mole ratio determined by the mean of the relative intensities of the triplet and the doublet ^{31}P NMR peaks.

Commercial $Fe(CO)_5$ was converted to $Fe_2(CO)_9$[9] and $Fe_3(CO)_{12}$[10] by the cited published procedures. The cyclotriphosphine $t\text{-}Bu_3P_3$ was prepared from $t\text{-}BuCl$, Mg, and PCl_3 through $t\text{-}BuPCl_2$ using published procedures.[11,12]

Before use, all solvents were distilled under dry nitrogen over appropriate drying agents (sodium benzophenone ketyl or metal hydrides except for chlorinated solvents). Air-sensitive organometallic and organophosphorus compounds were handled in a dry nitrogen atmosphere.

Reactions of $t\text{-}Bu_3P_3$ with Iron Carbonyls. (a) Iron Pentacarbonyl. A solution of 4.65 g (17.6 mmol) of $t\text{-}Bu_3P_3$ and 7.1 mL (52.8 mmol) of $Fe(CO)_5$ in 500 mL of toluene was boiled under reflux for 24 h. Solvent and other volatile materials were removed under vacuum. The residue was extracted with 200 mL of hexane. Concentrating and cooling the extract gave some black-yellow crystals which were washed with three 20-mL portions of hexane and dried to give 0.90 g (9.4% yield) of brown-yellow, slightly air-sensitive crystalline $t\text{-}Bu_3P_3Fe_2(CO)_6$ (II; R = *tert*-butyl), 200–201 °C (dec). Anal. Calcd for $C_{18}H_{27}Fe_2O_6P_3$: C, 39.7; H, 5.0. Found: C, 39.7; H, 4.9.

(b) Diiron Enneacarbonyl. A mixture of 7.83 g (29.6 mmol) of $t\text{-}Bu_3P_3$ and 21.6 g (59 mmol) of $Fe_2(CO)_9$ in 500 mL of hexane was stirred for 24 h at room temperature. Concentration and cooling in a −10 °C freezer for 1 week gave 1.19 g (5.6% yield) of brown-yellow crystalline $t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$, 140–143 °C (dec). Anal. Calcd for $C_{22}H_{27}Fe_3O_{10}P_3$: C, 37.1; H, 3.8. Found: C, 36.9; H, 4.2. Chromatography of the filtrate from the reaction between $Fe_2(CO)_9$ and $t\text{-}Bu_3P_3$ yielded an amorphous brown solid exhibiting ^{31}P NMR resonances at δ −19.8 (apparent quintet, separations ~60 Hz) and δ −79.4 (double triplet, J_D = ~260 Hz; J_T = ~60 Hz); suitable single crystals of this product could not be obtained.

Reactions of $t\text{-}Bu_3P_3$ with $Fe_2(CO)_9$ were carried out under a variety of conditions and the resulting mixtures were analyzed for the relative amounts of $t\text{-}Bu_3P_3Fe_2(CO)_6$ and $t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$ by ^{31}P NMR; the results are tabulated in Table III.

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Table IV. Crystal Data for $t\text{-}Bu_3P_3Fe_2(CO)_6$ and $t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$

	$t\text{-}Bu_3P_3Fe_2(CO)_6$	$t\text{-}Bu_3P_3$ $[Fe(CO)_4]Fe_2(CO)_6$
formula	$C_{18}H_{27}Fe_2O_6P_3$	$C_{22}H_{27}Fe_3O_{10}P_3$
mol wt	544.03	683.91
cryst dimensions, mm	0.20 × 0.25 × 0.50	0.075 × 0.225 × 0.25
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$
a, Å	10.522 (5)	9.180 (5)
b, Å	12.188 (4)	16.923 (7)
c, Å	19.807 (8)	19.186 (9)
β, deg	90	93.27 (4)
V, Å^3	2540 (1)	2975 (7)
$F(000)$	1120	1392
μ(Cu Kα), cm^{-1}	112.9	135.8
transmission factors, %	67.21 to 99.45	33.78 to 99.51
D_{calcd}, g cm^{-1}	1.423	1.526
Z	4	4
no. of total reflcns	2932	6330
no. of obsd reflcns	1471	2604
octants collcd	$+h, +k, +l$	$+h, +k, \pm l$
max 2θ, deg	150.0	150.0
R^a	0.057	0.062
$R_w{}^a$	0.076	0.080

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w_i(||F_{o_i}| - |F_{c_i}||)^2/\sum w_i|F_{o_i}|^2]^{1/2}$.

(c) Triiron Dodecacarbonyl. A mixture of 3.6 g (13.6 mmol) of $t\text{-}Bu_3P_3$ and 6.9 g (13.7 mmol) of $Fe_3(CO)_{12}$ in 150 mL of benzene was boiled under reflux for 24 h. After removal of solvent under vacuum the residue was extracted with 100 mL of hexane. Cooling the hexane extract in the refrigerator for 10 h gave 1.58 g (21% yield) of brown crystalline $t\text{-}Bu_3P_3Fe_2(CO)_6$.

Reactions of $t\text{-}Bu_3P_3Fe_2(CO)_6$. (a) Oxidation with Hydrogen Peroxide. A solution of 0.77 g (1.4 mmol) of $t\text{-}Bu_3P_3Fe_2(CO)_6$ and 0.3 mL (2.8 mmol) of 30% hydrogen peroxide in 100 mL of ethanol and 5 mL of hexane was stirred for 30 min at 0 °C and then 3.5 h at room temperature. Solvents and excess H_2O_2 were removed under vacuum. The residue was extracted with 100 mL of a 6:1 hexane/CH_2Cl_2 mixture. Concentration of the extract at 20 mm gave 0.83 g (99% yield) of yellow crystalline air-stable $t\text{-}Bu_3P_3OFe_2(CO)_6$, 220–223 °C (dec). Anal. Calcd for $C_{18}H_{27}Fe_2O_7P_3$: C, 38.6; H, 4.9. Found: C, 38.4; H, 4.9.

(b) Reaction with Sulfur. A mixture of 5.3 g (9.7 mmol) of $t\text{-}Bu_3P_3Fe_2(CO)_6$, 0.4 g (1.6 mmol) of S_8, and 500 mL of toluene was boiled under reflux for 24 h. Removal of solvent from the filtered solution followed by crystallization of the residue from a 10:1 hexane/CH_2Cl_2 mixture gave 1.18 g (21% yield) of yellow $t\text{-}Bu_3P_3SFe_2(CO)_6$, 190–191 °C (dec). Anal. Calcd for $C_{18}H_{27}Fe_2O_6P_3S$: C, 37.5; H, 4.7. Found: C, 37.6; H, 4.7.

(c) Reaction with $Fe_2(CO)_9$. A mixture of 0.37 g (0.68 mmol) of $t\text{-}Bu_3P_3Fe_2(CO)_6$ and 0.50 g (1.36 mmol) of $Fe_2(CO)_9$ in 80 mL of hexane was stirred at room temperature for 24 h. Phosphorus-31 NMR of the reaction mixture indicated the presence of a ~1:1 mixture of $t\text{-}Bu_3P_3Fe[Fe(CO)_4]Fe_2(CO)_6$ and unchanged $t\text{-}Bu_3P_3Fe_2(CO)_6$.

(d) Reaction with (thf)$Cr(CO)_5$. An orange tetrahydrofuran solution of (thf)$Cr(CO)_5$ was generated by photolysis of 1.1 g (5 mmol) of $Cr(CO)_6$ in 450 mL of tetrahydrofuran for 5 h. After 2.27 g (4.17 mmol) of $t\text{-}Bu_3P_3Fe_2(CO)_6$ was added to this solution, the reaction mixture was stirred at room temperature for 10 h. Removal of solvent and $Cr(CO)_6$ under vacuum followed by extraction with a mixture of hexane (300 mL) and dichloromethane (10 mL), evaporation of the extract, removal of more $Cr(CO)_6$ at 75 °C/0.03 mm, and crystallization from hexane resulted in the isolation of unchanged $t\text{-}Bu_3P_3Fe_2(CO)_6$, identified by phosphorus-31 NMR.

Structure Determinations of $t\text{-}Bu_3P_3Fe_2(CO)_6$ and $t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$ (Table IV). Orange needle crystals of $t\text{-}Bu_3P_3Fe_2(CO)_6$ and $t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$ from hexane were fixed in a random orientation on a glass fiber and mounted on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite crystal monochromator and Cu K_α irradiation (1.541 84 Å). Cell dimensions were determined by least-squares refinement of the angular positions of 25 independent reflections for each sample in the 15–25° θ range during the normal alignment procedure. Intensity data were collected at ambient temperature over a θ range of 2–75° using the ω–2θ technique with a variable scan width and scan range. A semiempirical absorption correction[13] was applied to each data set. Table IV provides information relevant to the crystal cells and data collections.

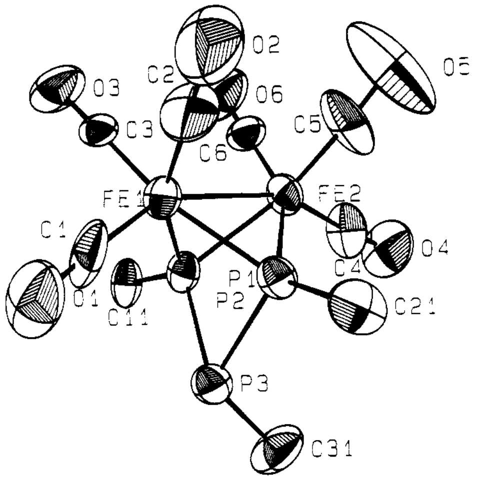

Figure 1. ORTEP diagram of $t\text{-}Bu_3P_3Fe_2(CO)_6$. The nine methyl groups are omitted for clarity.

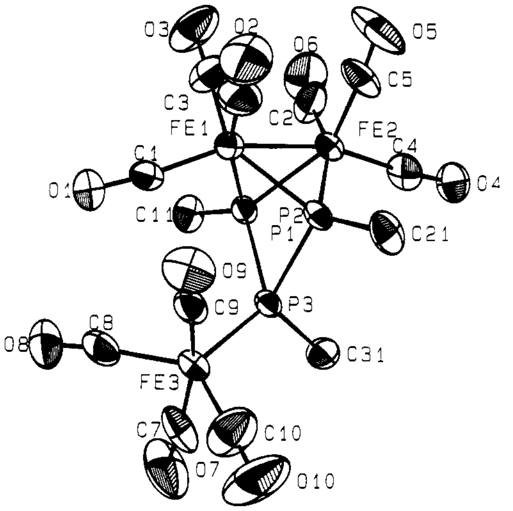

Figure 2. ORTEP diagram of $t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$. The nine methyl groups are omitted for clarity.

Table V. Selected Bond Distances (Å) for $t\text{-}Bu_3P_3Fe_2(CO)_6$

Fe1–Fe2	2.602 (3)	Fe2–P2	2.243 (5)
Fe1–P1	2.229 (4)	Fe2–C4	1.71 (2)
Fe1–P2	2.235 (5)	Fe2–C5	1.76 (2)
Fe1–C1	1.74 (2)	Fe2–C6	1.76 (1)
Fe1–C2	1.72 (2)	P1–P2	2.499 (6)
Fe1–C3	1.77 (1)	P1–P3	2.226 (6)
Fe2–P1	2.234 (4)	P2–P3	2.209 (6)

The structural analyses were performed on a VAX 6210 using the MolEN structure analysis program system.[14] The structures were solved using SIR88 with eight symbols.[15] All non-hydrogen atoms were located in several difference Fourier maps and then refined by full-matrix least-squares, first isotropically, then anisotropically. Hydrogens were not included in the analysis of the structures. The final unweighted R values were 0.057 for $t\text{-}Bu_3P_3Fe_2(CO)_6$ and 0.062 for $t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$.

The structures of $t\text{-}Bu_3P_3Fe_2(CO)_6$ and $t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$ are depicted in Figures 1 and 2, respectively. Selected bond distances and angles of $t\text{-}Bu_3P_3Fe_2(CO)_6$ and $t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$ are depicted in Tables V–VIII.

Results

Reaction of $t\text{-}Bu_3P_3$ with either $Fe(CO)_5$ in boiling toluene or $Fe_3(CO)_{12}$ in boiling benzene gave a brown-yellow crystalline

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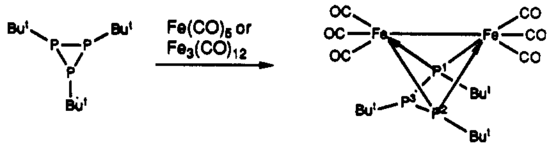
Table VI. Selected Bond Angles (deg) for *t*-$Bu_3P_3Fe_2(CO)_6$

Fe2–Fe1–P1	54.4 (1)	Fe1–P1–Fe2	71.3 (1)
Fe2–Fe1–P2	54.6 (1)	Fe1–P1–P2	56.1 (1)
Fe2–Fe1–C1	151.2 (6)	Fe1–P1–P3	93.3 (2)
Fe2–Fe1–C2	97.6 (8)	Fe1–P1–C21	128.8 (6)
Fe2–Fe1–C3	103.8 (5)	Fe2–P1–P2	56.2 (1)
P1–Fe1–P2	68.1 (2)	Fe2–P1–P3	105.1 (2)
P1–Fe1–C1	100.5 (6)	Fe2–P1–C21	133.0 (6)
P1–Fe1–C2	99.1 (7)	P2–P1–P3	55.4 (2)
P1–Fe1–C3	158.0 (5)	P2–P1–C21	169.2 (5)
P2–Fe1–C1	105.9 (6)	P3–P1–C21	113.8 (5)
P2–Fe1–C2	152.8 (8)	Fe1–P2–Fe2	71.0 (1)
P1–Fe1–C3	97.5 (5)	Fe1–P2–P1	55.8 (1)
C1–Fe1–C2	101 (1)	Fe1–P2–P3	93.7 (2)
C1–Fe1–C3	99.5 (8)	Fe1–P2–C11	129.2 (5)
C2–Fe1–C3	86.2 (8)	Fe2–P2–P1	55.9 (1)
Fe1–Fe2–P1	54.2 (1)	Fe2–P2–P3	105.4 (2)
Fe1–Fe2–P2	54.3 (1)	Fe2–P2–C11	130.8 (5)
Fe1–Fe2–C4	156.0 (6)	P1–P2–P3	56.0 (2)
Fe1–Fe2–C5	100.3 (6)	P1–P2–C11	171.4 (5)
Fe1–Fe2–C6	97.6 (5)	P3–P2–C11	115.4 (5)
P1–Fe2–P2	67.9 (2)	P1–P3–P2	68.6 (2)
P1–Fe2–C4	108.6 (6)	P1–P3–C31	116.1 (7)
P1–Fe2–C5	95.6 (6)	P2–P3–C31	113.7 (6)
P1–Fe2–C6	151.5 (5)	Fe1–C1–O1	177 (2)
P2–Fe2–C4	105.6 (6)	Fe1–C2–O2	179 (2)
P2–Fe2–C5	154.3 (6)	Fe1–C3–O3	178 (1)
P2–Fe1–C6	93.2 (5)	Fe2–C4–O4	175 (1)
C4–Fe2–C5	97.9 (8)	Fe2–C5–O5	177 (1)
C4–Fe2–C6	96.6 (8)	Fe2–C6–O6	178 (1)
C5–Fe2–C6	94.1 (8)		

Table VII. Selected Bond Distances (Å) for *t*-$Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$

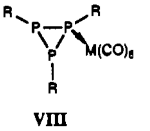
Fe1–Fe2	2.581 (2)	Fe2–C6	1.78 (1)
Fe1–P1	2.252 (3)	Fe3–P3	2.281 (3)
Fe1–P2	2.263 (3)	Fe3–C7	1.75 (1)
Fe1–C1	1.77 (1)	Fe3–C8	1.83 (1)
Fe1–C2	1.72 (1)	Fe3–C9	1.79 (1)
Fe1–C3	1.77 (1)	Fe3–C10	1.80 (1)
Fe2–P1	2.248 (3)	P1–P2	2.527 (3)
Fe2–P2	2.251 (3)	P1–P3	2.250 (4)
Fe2–C4	1.77 (1)	P2–P3	2.242 (4)
Fe2–C5	1.76 (1)		

essentially air-stable product *t*-$Bu_3P_3Fe_2(CO)_6$ as the only organophosphorus iron carbonyl derivative detected by ^{31}P NMR. The yield of this product was significantly better under the milder conditions used for the $Fe_3(CO)_{12}$ reaction. The structure (Figure 1) of *t*-$Bu_3P_3Fe_2(CO)_6$ was shown by X-ray diffraction to be the expected VII (≡II: R = *tert*-butyl) in which one of the three P–P bonds in the cyclotriphosphine ring of *t*-Bu_3P_3 has been cleaved according to the following general scheme:



VII ≡ II: R = *tert*-butyl

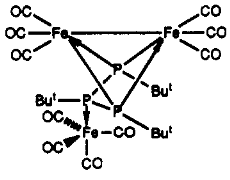
Important features (Table V) of the structure of VII include the Fe–Fe bond (2.602 Å), the P–P bonding distances of 2.226 (8) and 2.209 (6) Å between P1 and P3 and between P2 and P3, respectively, and the P–P distance of 2.499 (6) Å between P1 and P2. This P1–P2 distance is about 0.3 Å longer than a P–P single bond distance and to a first approximation can be interpreted as a nonbonding P–P distance. However, nonparametrized molecular orbital calculations by Teo, Hall, Fenske, and Dahl[16] on related binuclear iron carbonyl complexes suggest a small amount of residual P···P attractive interaction in such structures. The essentially equilateral (60 ± 1° angles) triangle geometry[17] of the starting cyclotriphosphine *t*-Bu_3P_3 is perturbed relatively little (i.e., to a triangle with angles of 56.56 (6)°, 68.19 (7)°, and 55.25 (6)° with no angles deviating by more than 8° from an equilateral triangle—see Table IX) upon cleavage of one of its P–P bonds by reaction with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ to give VII. In addition the observed P–P bond cleavage upon reaction of *t*-Bu_3P_3 with the iron carbonyls contrasts with the lack of P–P bond cleavage in the reported complexation of *t*-Bu_3P_3 with a $Cr(CO)_5$ unit to form *t*-$Bu_3P_3Cr(CO)_5$ (VIII: R = *t*-Bu, M = Cr)[18,19] or of *i*-Pr_3P_3 with a $W(CO)_5$ unit to form *i*-$Pr_3P_3W(CO)_5$ (VIII: R = *i*-Pr, M = W)[20] in which all three P–P bonds of the cyclotriphosphine ring are retained and the P–P–P angles are within ±1° of the 60° values for an equilateral triangle (Table IX). The geometry of the P_3 unit in *t*-$Bu_3P_3Fe_2(CO)_6$ (VII) is also similar to that of the P_3 units in the related compounds (*i*-$Pr_2NP)_3Fe_2(CO)_6$ (II: R = *i*-Pr_2N),[2] (*i*-$Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$ (IV),[4] (*i*-$Pr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$,[4] and $Ph_2P_3[Fe_2(CO)_6(\mu_2\text{-}PPh_2)]Fe_2(CO)_6$ (VI)[6] listed in Table IX.



VIII

The spectroscopic properties of *t*-$Bu_3P_3Fe_2(CO)_6$ are in accord with structure VII. Thus the infrared spectrum (Table I) shows only terminal carbonyl frequencies and is very similar to that of the related compound (*i*-$Pr_2NP)_3Fe_2(CO)_6$ (II: R = *i*-Pr_2N). The phosphorus-31 NMR spectrum (Table I) shows the expected AX_2 pattern consisting of a doublet and a triplet with a $|^1J(P\text{–}P)|$ of 264 Hz. The proton and carbon-13 NMR spectra indicate the presence of two types of *tert*-butyl groups as required by structure VII.

The reaction of *t*-Bu_3P_3 with $Fe_2(CO)_9$ under milder conditions was found to be somewhat more complicated than the reactions of *t*-Bu_3P_3 with $Fe(CO)_5$ or $Fe_3(CO)_{12}$. Three organophosphorus iron carbonyl products were observed: (1) *t*-$Bu_3P_3Fe_2(CO)_6$ (VII); (2) an amorphous brown product which could not be characterized but which exhibited distinctive multiplet ^{31}P resonances at δ −19 and δ −79; (3) *t*-$Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$ shown by X-ray diffraction to have structure IX (Figure 2). Structure IX is closely related to that of t-$Bu_3P_3Fe_2(CO)_6$ (VII) with an $Fe(CO)_4$ unit being bonded to the central phosphorus atom (P^3) in VII. Thus the geometries of the *t*-$Bu_3P_3Fe_2(CO)_6$ units in VII and IX are very similar (Tables V–VIII). The mole ratio of *t*-$Bu_3P_3Fe_2(CO)_6$ to *t*-$Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$ formed in the reaction of *t*-Bu_3P_3 with $Fe_2(CO)_9$ (as determined by ^{31}P NMR) depends significantly upon the reaction conditions (Table III); higher temperatures and/or more polar solvents (e.g., tetrahydrofuran relative to diethyl ether) favored formation of the diiron complex VII rather than the triiron complex IX. Also heating solid IX to ~180 °C led to significant decomposition resulting in loss of the $Fe(CO)_4$ group to give VII as indicated by the ^{31}P NMR spectrum.



IX

The isolation of IX from the reaction of *t*-Bu_3P_3 with $Fe_2(CO)_9$ indicates the activity of the lone pair on the central phosphorus atom (P^3) in *t*-$Bu_3P_3Fe_2(CO)_6$ (VII) with the source of the $Fe(CO)_4$ group being the well-known dissociation of $Fe_2(CO)_9$ under mild conditions to stable $Fe(CO)_5$ and a reactive $Fe(CO)_4$ fragment by the process

$$Fe_2(CO)_9 \rightarrow Fe(CO)_5 + \{Fe(CO)_4\} \qquad (2)$$

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Table VIII. Selected Bond Angles (deg) for $t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$

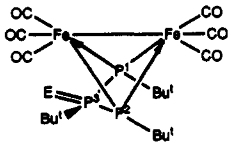
Fe2–Fe1–P1	54.93 (8)	Fe1–Fe2–C6	108.3 (4)	C9–Fe3–C10	87.5 (6)	P1–P2–C21	171.2 (4)
Fe2–Fe1–P2	54.91 (8)	P1–Fe2–P2	68.4 (1)	Fe1–P1–Fe2	70.00 (9)	P3–P2–C21	117.3 (3)
Fe2–Fe1–C1	152.9 (3)	P1–Fe2–C4	120.5 (3)	Fe1–P1–P2	56.16 (9)	Fe3–P3–P1	123.7 (1)
Fe2–Fe1–C2	112.6 (4)	P1–Fe2–C5	142.2 (4)	Fe1–P1–P3	95.8 (1)	Fe3–P3–P2	116.0 (1)
Fe2–Fe1–C3	85.3 (4)	P1–Fe2–C6	93.3 (4)	Fe1–P1–C11	123.2 (4)	Fe3–P3–C31	115.9 (3)
P1–Fe1–P2	68.1 (1)	P2–Fe2–C4	101.1 (4)	Fe2–P1–P2	55.87 (9)	P1–P3–P2	68.5 (1)
P1–Fe1–C1	97.9 (3)	P2–Fe2–C5	96.2 (4)	Fe2–P1–P3	104.1 (1)	P1–P3–C31	109.4 (3)
P1–Fe1–C2	164.4 (4)	P2–Fe2–C6	160.1 (4)	Fe2–P1–C11	131.2 (3)	P2–P3–C31	115.0 (3)
P1–Fe1–C3	97.6 (4)	C4–Fe2–C5	95.7 (5)	P2–P1–P3	55.6 (1)	Fe1–C1–O1	173 (1)
P2–Fe1–C1	119.3 (4)	C4–Fe2–C6	94.8 (5)	P2–P1–C11	118.9 (4)	Fe1–C2–O2	178 (1)
P2–Fe1–C2	97.3 (4)	C5–Fe2–C6	94.1 (6)	Fe1–P2–Fe2	69.8 (1)	Fe1–C3–O3	179 (1)
P2–Fe1–C3	139.3 (4)	P3–Fe3–C7	99.1 (4)	Fe1–P2–P1	55.76 (9)	Fe2–C4–O4	174 (1)
C1–Fe1–C2	94.1 (5)	P3–Fe3–C8	121.1 (4)	Fe1–P2–P3	95.7 (1)	Fe2–C5–O5	176 (1)
C1–Fe1–C3	99.8 (5)	P3–Fe3–C9	95.6 (3)	Fe1–P2–C21	132.8 (4)	Fe2–C6–O6	172 (1)
C2–Fe1–C3	90.1 (6)	P3–Fe3–C10	114.0 (5)	Fe2–P2–P1	55.77 (9)	Fe3–C7–O7	174 (1)
Fe1–Fe2–P1	55.07 (8)	C7–Fe3–C10	87.5 (6)	Fe2–P2–P3	104.3 (1)	Fe3–C8–O8	174 (1)
Fe1–Fe2–P2	55.33 (8)	C8–Fe3–C9	86.0 (5)	Fe2–P2–C21	125.9 (3)	Fe3–C9–O9	175.2 (9)
Fe1–Fe2–C4	156.4 (3)	C8–Fe3–C10	124.8 (6)	P1–P2–P3	55.9 (1)	Fe3–C10–O10	177 (1)
Fe1–Fe2–C5	87.5 (4)						

Table IX. Dimensions of the Triphosphine Unit in Metal Carbonyl Complexes

	P–P distances,[a] Å			P–P–P angles,[a] deg			
compound	1–2	1–3	2–3	1–2–3	2–3–1	3–1–2	lit.
$(i\text{-}Pr_2NP)_3Fe_2(CO)_6$	2.534 (2)	2.278 (2)	2.243 (2)	56.56 (6)	68.19 (7)	55.25 (6)	2
$(i\text{-}Pr_2NP)_2P(Cl)[Cr(CO)_5]Fe_2(CO)_6$	2.603 T	2.240 (3)	2.246 (2)		70.94 (8)		4
$(i\text{-}Pr_2NP)_2P[Mn(CO)_5]Fe_2(CO)_6$	2.513 T	2.235 (4)	2.231 (4)		68.5 (1)		4
$t\text{-}Bu_3P_3$	2.187 (1)	2.185 (2)	2.213 (2)	59.6 (1)	59.6 (1)	60.8 (1)	17
$t\text{-}Bu_3P_3Cr(CO)_5$	2.194 (2)	2.211 (2)	2.191 (2)	60.73 (7)	59.69 (7)	59.58 (7)	20
$i\text{-}Pr_3P_3W(CO)_5$	2.181 (4)	2.188 (3)	2.207 (4)	59.8 T	59.5 T	60.7 T	20
$t\text{-}Bu_3P_3Fe_2(CO)_6$	2.499 (6)	2.226 (6)	2.209 (6)	56.0 (2)	68.6 (2)	55.4 (2)	this work
$t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$	2.527 (3)	2.250 (4)	2.242 (3)	55.9 (1)	68.5 (1)	55.6 (1)	this work
$Ph_2P_3[Fe_2(CO)_6(\mu_2\text{-}PPh_2)]Fe_2(CO)_6$ (VI)[b]	2.558 T	2.245 (2)	2.250 (2)		69.37 (6)		6
	2.528 T	2.247 (2)	2.300 (2)		67.57 (6)		

[a] T = distance or angle estimated by trigonometry from the reported data rather than taken directly from the cited papers. [b] Data are presented for two crystallographically independent molecules of VI in the unit cell.[6] The numbering of the phosphorus atoms in VI is changed to conform to the number of the other derivatives in Table IX.

Some other reactions of VII were investigated in order to assess the reactivity of the lone pair on P^3 of VII. Reaction of pure $t\text{-}Bu_3P_3Fe_2(CO)_6$ (VII) with $Fe_2(CO)_9$ in hexane or tetrahydrofuran at room temperature resulted in some complexation of P^3 in VII to give IX as indicated by ^{31}P NMR but leading to $t\text{-}Bu_3P_3Fe_2(CO)_6/t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$ ratios no lower than ~1 indicating some difficulty in this reaction proceeding to completion. Reaction of $t\text{-}Bu_3P_3Fe_2(CO)_6$ (VII) with $(thf)Cr(CO)_5$ resulted in no evidence (by ^{31}P NMR) for any complexation of P^3 in VII to an $Cr(CO)_5$ group. However, reaction of $t\text{-}Bu_3P_3Fe_2(CO)_6$ (VII) with hydrogen peroxide and with sulfur led to formation of the corresponding oxide (X: E = O) and sulfide (X: E = S), respectively, as indicated by the ^{31}P NMR and elemental analyses.



X

Discussion

The results described in this paper represent the first reported example of the cleavage of a cyclotriphosphine ring by a metal carbonyl derivative to give a linear triphosphine complex, namely $t\text{-}Bu_3P_3Fe_2(CO)_6$ (VII). The two outer phosphorus atoms in the P_3 chain in VII are each bonded to both metal atoms, whereas the central phosphorus atom remains trivalent and thus has a lone pair. Studies on the chemical reactivity of this lone pair indicate that it is reactive but only to a limited extent, possibly because of the steric hindrance of the *tert*-butyl groups. Thus although $t\text{-}Bu_3P_3Fe_2(CO)_6$ can readily be converted to the corresponding oxide and sulfide, attempts to complex an $Fe(CO)_4$ group to the central phosphorus atom (e.g., by reaction with $Fe_2(CO)_9$) do not go to completion and attempts to complex a $Cr(CO)_5$ group to the central phosphorus atom with $(thf)Cr(CO)_5$ were unsuccessful. By comparison our efforts to complex the central phosphorus atom in $(i\text{-}Pr_2NP)_3Fe_2(CO)_6$ with metal carbonyl moieties were also unsuccessful apparently because of the steric hindrance of the diisopropylamino group.[4] However, replacement of the diisopropylamino group on the central phosphorus atom in II (R = $i\text{-}Pr_2N$) with the less sterically demanding chlorine atom to give V was found to make the lone pair on the central phosphorus atom more accessible so that IV could be obtained by reaction of V with $(thf)Cr(CO)_5$.[4] In addition, $Cx_3P_3[Cr(CO)_5]Fe_2(CO)_6$ (III), which is closely related to IV, is reported[3] as a product from the reaction of $(CxPCl_2)Fe(CO)_4$ with $Na_2Cr_2(CO)_{10}$.

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Supplementary Material Available: Listings of positional parameters and their estimated standard deviations, anisotropic displacement factors, bond distances (Å), and bond angles (deg) for $t\text{-}Bu_3P_3Fe_2(CO)_6$ and $t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$ (Tables S1–S8) and labeled PLUTO diagrams and views of the unit cells for $t\text{-}Bu_3P_3Fe_2(CO)_6$ and $t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$ (19 pages); listings of observed and calculated structure factors for $t\text{-}Bu_3P_3Fe_2(CO)_6$ and $t\text{-}Bu_3P_3[Fe(CO)_4]Fe_2(CO)_6$ (47 pages).