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Complexes of Trivalent Phosphorus Derivatives. XVII. Reactions of Iron Carbonyls with 1,2,3-Triphenyl-1,2,3-triphosphaindane[1]

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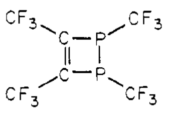
The reaction of $Fe_3(CO)_{12}$ with 1,2,3-triphenyl-1,2,3-triphosphaindane under various conditions gives a complex mixture of products from which the following compounds have been isolated: (1) pale yellow $C_6H_4(PC_6H_5)_3[Fe(CO)_4]_2$ in which $Fe(CO)_4$ units are coordinated to two phosphorus atoms of an intact 1,2,3-triphosphaindane ring; (2) a yellow to red isomer of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ (isomer A) in which one phosphorus–phosphorus bond of the 1,2,3-triphosphaindane ring is cleaved and only the two phosphorus atoms at each end of this cleaved phosphorus–phosphorus bond are directly bonded to iron atoms in the $Fe_3(CO)_9$ unit; (3) a dark red isomer of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ (isomer B) derived from isomer A by shift of an iron–phosphorus bond so that all three phosphorus atoms of the singly cleaved 1,2,3-triphosphaindane ring are directly bonded to iron atoms in the $Fe_3(CO)_9$ triangle; (4) an orange isomer of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ (isomer C) containing an intact 1,2,3-triphosphaindane ring with all three phosphorus atoms of this ring coordinated to iron atoms in the $Fe_3(CO)_9$ triangle; (5) pale yellow $C_6H_4(PC_6H_5)_2Fe_2(CO)_6$ formed by extrusion of a C_6H_5P unit from the 1,2,3-triphenylphosphaindane ring. Proton-decoupled phosphorus-31 NMR spectroscopy was used to establish the structures of the above compounds.

Introduction

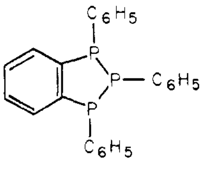
The chemistry of the interaction of phosphorus–phosphorus bonds with metal carbonyls originated in 1963 when two independent research groups[3,4] showed that reactions of tetraalkylbiphosphines, R_2PPR_2, with metal carbonyls could result either in retention of the phosphorus–phosphorus bond to give complexes with an intact tetraalkylbiphosphine ligand or in rupture of the phosphorus–phosphorus bond to give dialkylphosphido metal carbonyl derivatives. Subsequent work[5] has shown that an extensive series of dialkylphosphido metal carbonyl derivatives can be prepared by cleavage of the phosphorus–phosphorus bonds in various tetraalkylbiphosphines with metal carbonyls.

More recently, the study of reactions between metal carbonyls and compounds containing phosphorus–phosphorus bonds has been extended to cyclic derivatives with phosphorus–phosphorus bonds in the ring. Reactions of the homocyclic poly(alkylcyclopolyphosphines) (e.g., $(C_6H_5)_4P_4$) with metal carbonyls have been shown to result in either coordination of an intact cyclopolyphosphine ring,[6,7] coordination with ring cleavage involving rupture of one or more of the ring phosphorus–phosphorus bonds,[6,7] or coordination with concomitant ring expansion.[8-11] The chemistry of reactions of heterocyclic compounds containing phosphorus–phosphorus bonds with metal carbonyls appears to be limited to a report by Cowley and Hill[12] of the reaction of the fluorinated 1,2-diphospha-3-cyclobutene (I) with $Fe_2(CO)_9$ to give products of stoichiometries $(CF_3)_2P_2C_2(CF_3)_2Fe(CO)_4$ and $(CF_3)_2P_2C_2(CF_3)_2Fe_3(CO)_{10}$.

This paper describes the reactions of the heterocycle 1,2,3-triphenyl-1,2,3-triphosphaindane[13] ((II) also known[14] more cumbersomely as 2,3-dihydro-1,2,3-triphenyl-1*H*-1,2,3-benzotriphosphole) with iron carbonyls. These reactions gave several products of different types about which considerable structural information could be obtained by the use of proton-decoupled phosphorus-31 NMR spectroscopy. In this manner the products obtained from the reaction of $Fe_3(CO)_{12}$ with the 1,2,3-triphenyl-1,2,3-triphosphaindane (II) were shown to include compounds formed by coordination of the intact heterocycle, by rupture of a single phosphorus–phosphorus bond in the five-membered ring of II, and by extrusion of a C_6H_5P unit from the five-membered ring of II. Furthermore, sufficient information has been obtained on the structures and interconversions of the iron carbonyl complexes to deduce reaction pathways containing several unusual and unprecedented features which may be generally applicable to the chemistry of transition metal derivatives with phosphorus or sulfur bridges including possibly some metal–sulfur enzyme systems.[15] Metal complexes with RP units are useful as models for the chemistry of corresponding metal complexes with sulfur atoms to the extent that phosphorus-31 is a favorable spin $^1/_2$ isotope for structure elucidations by high-resolution NMR spectroscopy, particularly by modern Fourier transform techniques, whereas sulfur has no isotope with appropriate properties for high-resolution NMR spectroscopy.



I



II

Experimental Section

Reaction of 1,2,3-Triphenyl-1,2,3-triphosphaindane with $Fe_3(CO)_{12}$. A mixture of 8.0 g (16 mmol) of $Fe_3(CO)_{12}$,[16] 6.4 g (16 mmol) of 1,2,3-triphenyl-1,2,3-triphosphaindane,[13] and 150 ml of degassed toluene was boiled under reflux in a nitrogen atmosphere for 3 hr. Solvent was removed at ~25° (1 mm) leaving a black oil which was transferred to a 2 × 65 cm alumina chromatography column prepared in hexane. Elution of the column with 1:3 dichloromethane–hexane gave a crude separation of one strong orange band from a large quantity of insoluble black material. The product from the orange band was rechromatographed on a 2 × 80 cm alumina column prepared in hexane. Elution of this chromatogram with a 1:9 mixture of dichloromethane and hexane gave first a yellow band followed by a red band. Evaporation of the eluate from the red band followed by recrystallization from a mixture of dichloromethane and hexane gave large red needles of isomer B of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ (0.27 g, 2% yield). The product from the yellow band was shown by its infrared ν(CO) frequencies to be a complex mixture, which could not be further separated by column chromatography.

The entire product from the above yellow band was dissolved in 150 ml of hexane and the resulting solution was kept in a freezer at $-15°$. After 24 hr a mixture of large orange prisms of isomer C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ and a small quantity of $C_6H_4(PC_6H_5)_3Fe_2(CO)_8$ had crystallized out and were separated mechanically to give 0.77 g (6% yield) of isomer C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$. The filtrate from this crystallization was concentrated to 100 ml and then kept again at $-15°$. After about 24 hr a mixture of yellow microcrystalline isomer A of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ and yellow prisms of $C_6H_4(PC_6H_5)_3[Fe(CO)_4]_2$ precipitated. These were again separated mechanically and each compound recrystallized from a mixture of dichloromethane and hexane to give 1.66 g (14% yield) of $C_6H_4(PC_6H_5)_3[Fe(CO)_4]_2$ as pale yellow prisms and 1.18 g (9% yield) of isomer A of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ as a mixture of red prisms (isomer AR) and yellow plates (isomer AY). Both forms of isomer A had identical cyclohexane solution infrared spectra in the ν(CO)

Table I. Yields of Products from Triiron Dodecacarbonyl and 1,2,3-Triphenyl-1,2,3-triphosphaindane under Various Reaction Conditions

			Yields, %				
Solvent	Temp, °C	Time, hr	C_6H_4-$(PPh)_3$-[Fe-$(CO)_4]_2$	$C_6H_4(PPh)_3Fe_3$-$(CO)_9$ isomers A	B	C	C_6H_4-$(PPh)_2$-Fe_2-$(CO)_6$
Hexane	69	22	0	10	0.5	0	0
Benzene	80	17	11	8	0.5	0	0
Toluene	110	3	14	9	2	6	0
Toluene	110	24	0	0	1	28	3

region. A Nujol mull of isomer AR exhibited bands at 1310 (w), 1270 (vw), 1189 (w), 1163 (w), 1102 (m), 1099 (m), 1090 (w), 1075 (w), 1033 (vw), and 1004 (w) cm^{-1} whereas a Nujol mull of isomer AY exhibited bands at 1310 (w), 1267 (w), 1186 (vw), 1175 (vw), 1162 (vw), 1102 (m), 1090 (w), 1074 (w), 1030 (vw), and 1002 (m) cm^{-1} in their infrared spectra.

The filtrate after separation of isomer A of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ and $C_6H_4(PC_6H_5)_3[Fe(CO)_4]_2$ was still orange, but all further attempts at crystallization resulted in finely divided powders which were mixtures not amenable to mechanical separation.

By changing the conditions for the reaction between $Fe_3(CO)_{12}$ and 1,2,3-triphenyl-1,2,3-triphosphaindane the relative quantities of the different products varied as indicated in Table I. In the reactions carried out in hexane or benzene solutions, the methods for product isolation were similar to those described above. Although the yields given in Table I are rather imprecise estimates because of the difficulties in product isolation, the data indicate that mild conditions favor $C_6H_4(PC_6H_5)_3[Fe(CO)_4]_2$ and isomer A of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ whereas more vigorous conditions favor isomers B and C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$. No iron carbonyl derivatives containing units derived from 1,2,3-triphenyl-1,2,3-triphosphaindane were obtained by ultraviolet irradiation of $Fe_3(CO)_{12}$ with the heterocycle II in cyclohexane for 24 hr; the reaction mixture retained the deep green color characteristic of $Fe_3(CO)_{12}$. Infrared spectra of this reaction mixture indicated ~95% unchanged $Fe_3(CO)_{12}$.

The properties of the products obtained from the reactions of $Fe_3(CO)_{12}$ including their elemental analyses and molecular weight determinations are given in Table II.

Isolation of $C_6H_4(PC_6H_5)_2Fe_2(CO)_6$. A mixture of 5.6 g (11.0 mmol) of $Fe_3(CO)_{12}$, 4.0 g (10 mmol) of 1,2,3-triphenyl-1,2,3-triphosphaindane, and 40 ml of toluene was boiled under reflux in a nitrogen atmosphere for 24 hr. Solvent was then removed at 25° (1 mm). The residue was transferred to an alumina column prepared in hexane and the column eluted with a 1:1 mixture of dichloromethane and hexane. This removed an orange band from the column and left a relatively large amount of black solid material at the top. The eluate from the orange band was concentrated and rechromatographed on a 2 × 80 cm alumina column using 1:9 dichloromethane–hexane as the eluent. A very pale yellow fraction was first eluted. Evaporation of this eluate gave 0.18 g (3% yield) of yellow $C_6H_4(PC_6H_5)_2Fe_2(CO)_6$. Elution of the next orange band gave 1.7 g (28% yield) of isomer C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$. Elution of the following red band gave 0.1 g (1% yield) of isomer B of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$.

Heating a toluene solution of isomer B of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ at the boiling point for 20 hr gave mainly $C_6H_4(PC_6H_5)_2Fe_2(CO)_6$, identified by its infrared spectrum in the ν(CO) region.

Reaction of 1,2,3-Triphenyl-1,2,3-triphosphaindane with $Fe_2(CO)_9$. A mixture of 1.5 g (4.12 mmol) of $Fe_2(CO)_9$,[17] 1.65 g (4.12 mmol) of 1,2,3-triphenyl-1,2,3-triphosphaindane, and 100 ml of redistilled tetrahydrofuran was stirred for 6 hr at room temperature in a carbon monoxide atmosphere. After 6 hr the infrared spectrum of the solution in the ν(CO) region indicated that $C_6H_4(PC_6H_5)_3[Fe(CO)_4]_2$ was the only iron carbonyl species present. The product was isolated in ~45% yield, but could not be obtained completely pure unlike the corresponding reaction of II with $Fe_3(CO)_{12}$.

Infrared Spectra (Table III). Infrared spectra of the new compounds in the 2200–1600 cm^{-1} ν(CO) region (Table III) were run in cyclohexane solution and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Each spectrum was calibrated against the 1601-cm^{-1} band of polystyrene film. Table III also lists the ν(CO) frequencies of reported spectra of several compounds with arrangements of carbonyl groups similar to those in the proposed structures of the new compounds.

NMR Spectra (Table IV). The phosphorus-31 NMR spectra were taken in dichloromethane solution using a Jeolco PFT-100 spectrometer operating at 40.3 MHz in the Fourier transform mode with proton noise decoupling and a deuterium lock. The samples were placed in 10-mm NMR tubes also containing a concentric 5-mm tube of deuterium oxide for the lock and a capillary of 85% phosphoric acid for the standard. A pulse width of 90° was used with a repetition rate of 3 sec. Approximately 800 to 2000 such pulses were used to obtain a typical spectrum. The phosphorus-31 NMR chemical shifts are reported in ppm above the external 85% phosphoric acid standard.

The following proton NMR spectra were taken in C_6D_6 solution and recorded on a Varian HA-100 spectrometer at 100 MHz.

A. $C_6H_4(PC_6H_5)_3[Fe(CO)_4]_2$. Broad complex resonances at τ 1.9, 2.5, 2.9, 3.1, and 3.52 of approximate relative intensities 1:1:4:4:4, respectively.

B. Isomer C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_2$. Broad complex resonances at τ 2.0, 2.9, 3.1, and 3.5 of approximate relative intensities 2:4:1:1, respectively.

Results

The proton-decoupled phosphorus-31 ($^{31}P\{^1H\}$) NMR spectra were very important for elucidating the structures of the compounds prepared in this study since the ^1J(PP) for directly bonded phosphorus atoms is relatively large (~200 Hz) and thus readily identifiable from the spectra. For this reason, the $^{31}P\{^1H\}$ NMR spectra can be used to determine whether the phosphorus–phosphorus bonds in the triphosphaindane system of II have remained intact in its product with iron carbonyls or whether one (or conceivably both) of the phosphorus–phosphorus bonds in II is no longer present in the products.

The $^{31}P\{^1H\}$ NMR spectrum of the uncomplexed 1,2,3-

Table II. Properties of Products from Triiron Dodecacarbonyl and 1,2,3-Triphenyl-1,2,3-triphosphaindane

				Analyses, %			
Compd	Color and form	Mp, °C		C	H	O	Mol wt in benzene
$C_6H_4(PPh)_3[Fe(CO)_4]_2$	Pale yellow	195–197	Calcd	52.2	2.6	17.4	736
	prisms	dec	Found	52.3	2.7	17.6[a]	731
$C_6H_4(PPh)_3Fe_3(CO)_9$ (isomer A, red)	Red	179–184	Calcd	48.3	2.3	17.6	820
	prisms	dec	Found	48.4[a]	2.4[a]	17.8[a]	821
$C_6H_4(PPh)_3Fe_3(CO)_9$ (isomer A, yellow)[b]	Yellow	180–185	Calcd	48.3	2.3	17.6	820
	plates	dec	Found	48.2	2.3	17.6	823
$C_6H_4(PPh)_3Fe_3(CO)_9$ (isomer B)	Dark red	239–245	Calcd	48.3	2.3	17.6	820
	needles	dec	Found	48.5[a]	2.4[a]	17.7[a]	748
$C_6H_4(PPh)_3Fe_3(CO)_9$ (isomer C)	Orange	233–235	Calcd	48.3	2.3	17.6	820
		dec	Found	48.4[a]	2.4[a]	17.5[a]	817
$C_6H_4(PPh)_2Fe_2(CO)_6$	Pale yellow	200–201	Calcd	50.4	2.5	16.8	572
	plates	dec	Found	50.6[a]	2.5[a]	16.9	589

[a] The indicated values on these compounds are averages of determinations on two independent samples. [b] This compound retained solvent tenaciously and had to be dried at 90° (0.001 mm) before analysis.

Table III. Infrared ν(CO) Frequencies of the Products from Triiron Dodecacarbonyl and Related Model Compounds

Compd	Infrared spectra, cm^{-1}	
	Solvent	ν(CO)
$C_6H_4(PPh)_3[Fe(CO)_4]_2$	Cyclohexane	2048 s, 1980 s, 1949 vs
$Ph_3PFe(CO)_4$[a]	Hexane	2050 s, 1977 s, 1945 vs
$C_6H_4(PPh)_3Fe_3(CO)_9$ (isomer A, red)	Cyclohexane	2063 w, 2052 m, 2023 s, 1996 m, 1985 m, 1978 m, 1969 m, 1952 m
$C_6H_4(PPh)_3Fe_3(CO)_9$ (isomer B)	Cyclohexane	2064 m, 2031 s, 1996 s, 1979 w, 1970 m, 1960 m, 1954 m, 1942 w
$C_6H_4(PPh)_3Fe_3(CO)_9$ (isomer C)	Cyclohexane	2070 w, 2048 s, 2017 s, 1996 s, 1991 s, 1968 sh, 1962 m, 1952 m
$ffarsFe_3(CO)_9$[b]	Cyclohexane	2074 s, 2042 vs, 2021 vs, 2008 m, 1999 s, 1988 s, 1980 m, 1963 w
$As_2(CH_3)_2CH_2Fe_3(CO)_9$[b]	Cyclohexane	2066 w, 2039 vs, 2014 vs, 2000 vs, 1992 s, 1982 m, 1968 w, 1957 w
$C_6H_4(PPh)_2Fe_2(CO)_6$	Cyclohexane	2053 m, 2016 s, 1987 s, 1974 s, 1962 m
$[Me_2PFe(CO)_3]_2$[c]	CS_2	2050 s, 2010 vs, 1977 vs, 1962 vs

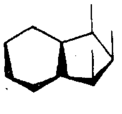
[a] Data of D. J. Darensbourg, H. H. Nelson, III, and C. L. Hyde, *Inorg. Chem.*, 13, 2135 (1974). [b] Data of W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, 9, 702 (1970). See that paper for the structures of these two complexes. [c] Data of R. G. Hayter, *Inorg. Chem.*, 3, 711 (1964).

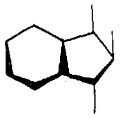
Table IV. Proton-Decoupled Phosphorus-31 NMR Spectra of New Compounds Prepared in This Work

Compd	Phosphorus-31 NMR, δ[a]		
	P^A in III or P^{AB} in V	P^B in III or V	P^{AA} in V
$C_6H_4(PPh)_3$	−32.3 d (251), −32.4 d (276)	+39.6 dd (276, 251)	
$C_6H_4(PPh)_3[Fe(CO)_4]_2$	−89.9 d (256), −90.0 d (270)	+28.5 dd (270, 256)	
$C_6H_4(PPh)_3Fe_3(CO)_9$ (A1)	−32.8 dd (237, 12)	−130.0 d (237)	−118.0 d (12)
$C_6H_4(PPh)_3Fe_3(CO)_9$ (A2)	−32.8 dd (237, 12)	−133.6 d (237)	−113.4 d (12)
$C_6H_4(PPh)_3Fe_3(CO)_9$ (B)	−55.7 d (267)	−116.5 dd (264, 22)	−74.4 d (22)
$C_6H_4(PPh)_3Fe_3(CO)_9$ (C)	+16.7 dd (183.5)	−55.6 dd (189, 178)	
$C_6H_4(PPh)_2Fe_2(CO)_6$			−138.1 s

[a] s = singlet, d = doublet, dd = double doublet; coupling constants in Hz are given in parentheses.

triphenyl-1,2,3-triphosphaindane (II) might be expected to exhibit a triplet corresponding to the single center phosphorus atom (P^B in III) and a doublet corresponding to the two equivalent phosphorus atoms adjacent to the ortho-disubstituted benzene ring (P^A in III). The actual pattern (Table IV) is slightly more complex probably owing to the possibility of three stereoisomers of II represented schematically as the cis,cis isomer IIa, the cis,trans isomer IIb, and the trans,trans isomer IIc. X-ray crystallography[18] shows crystalline 1,2,3-triphenyl-1,2,3-triphosphaindane (II) to be the trans,trans isomer IIc. However, our $^{31}P\{^1H\}$ NMR spectra of II show a double doublet with slightly different (276 and 251 Hz) $^1J_1(PP)$ and $^1J_2(PP)$ coupling constants for the single center phosphorus atom (P^B in III) and two closely spaced doublets of slightly different (~0.1 ppm) chemical shifts for the remaining two phosphorus atoms (P^A in III) which thus apparently are very slightly nonequivalent. This suggests that in solution 1,2,3-triphenyl-1,2,3-triphosphaindane (II) is the cis,trans isomer IIb, since this is the only one of the three possible stereoisomers for which the two phosphorus atoms directly bonded to the ortho-disubstituted benzene ring (P^A in III) are nonequivalent. In any case, precise interpretation of this fine structure of the $^{31}P\{^1H\}$ NMR spectrum of II is unimportant to the arguments presented in this paper. Under low resolution conditions (resolution ~20 Hz) as found in a reported[14] undecoupled phosphorus-31 NMR spectrum of II the observed $^{31}P\{^1H\}$ NMR spectrum collapses to the simple 1:2:1 triplet and 1:1 doublet for two equivalent phosphorus atoms strongly coupled to a third phosphorus atom which would be expected for II in the absence of effects from the specific stereoisomers IIa, IIb, and IIc.


IIa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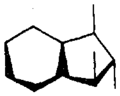
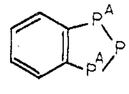
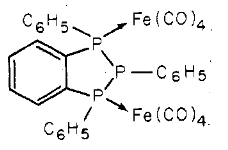

IIc

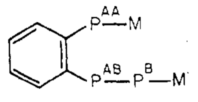


III

The product $C_6H_4(PC_6H_5)_3[Fe(CO)_4]_2$ appears to retain the 1,2,3-triphosphaindane ring system without cleavage of any phosphorus−phosphorus bonds. Its $^{31}P\{^1H\}$ NMR spectrum exhibits the same pattern as the free 1,2,3-triphenyl-1,2,3-triphosphaindane (II). The resonance centered at −32.3 ppm in the free ligand II corresponding to the two equivalent phosphorus atoms (P^A in III) is shifted downfield to −90.0 ppm in the bis(iron tetracarbonyl) complex whereas the resonance centered at +39.6 ppm in II corresponding to the center phosphorus atom (P^B in III) is shifted only slightly to +28.5 ppm in the bis(iron tetracarbonyl) complex. These $^{31}P\{^1H\}$ NMR data are interpreted on the basis of structure IV for $C_6H_4(PC_6H_5)_3[Fe(CO)_4]_2$ in which both ligand phosphorus atoms adjacent to the ortho-disubstituted benzene ring (P^A in III) are coordinated to $Fe(CO)_4$ units but the center ligand phosphorus atom (P^B in III) is uncoordinated. Further evidence for this structure IV of $C_6H_4(PC_6H_5)_3[Fe(CO)_4]_2$ comes from the close similarities in the patterns of the infrared ν(CO) frequencies in $C_6H_4(PC_6H_5)_3[Fe(CO)_4]_2$ and the simple triphenylphosphine complex $(C_6H_5)_3PFe(CO)_4$ and from the formation of $C_6H_4(PC_6H_5)_3[Fe(CO)_4]_2$ as the predominant product from the reaction of 1,2,3-triphenyl-1,2,3-triphosphaindane (II) with $Fe_2(CO)_9$ in tetrahydrofuran. Recent work[19] has shown $Fe_2(CO)_9$ in tetrahydrofuran to be an excellent source of reactive $Fe(CO)_4$ groups under mild conditions.



IV

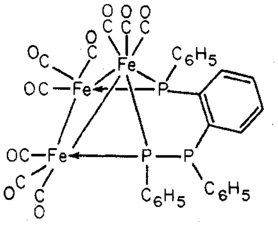


V

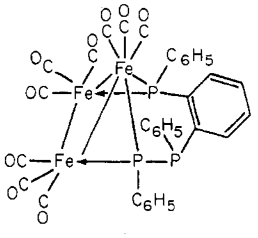
The structures of the three isomers of stoichiometry $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ pose a considerably more complex problem. The infrared spectrum in the ν(CO) region of each of these three isomers indicates the absence of bridging carbonyl groups and resembles the infrared spectra of other $Fe_3(CO)_9$ derivatives without bridging carbonyl groups (Table III). Furthermore, molecular weight determinations in benzene solution indicate formulations with three iron atoms rather than more complex formulations with multiples of three iron atoms. The $^{31}P\{^1H\}$ NMR spectrum of isomer B of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ exhibits the expected three resonances. Two of these resonances (−55.7 and −116.5 ppm) are split into doublets by a large coupling (~265 Hz) corresponding to the ^1J(PP) of two directly bonded phosphorus atoms. One of these doublets (−116.5 ppm) is further split (22 Hz) by a much smaller phosphorus–phosphorus coupling. This smaller 22-Hz coupling is reflected in the third phosphorus resonance (−74.4 ppm) which does not contain any large coupling thus indicating that this phosphorus atom is not directly bonded to either of the other two phosphorus atoms. This indicates that exactly one of the phosphorus–phosphorus bonds in the heterocycle II has been cleaved to form a unit of structure V in its reaction with $Fe_3(CO)_{12}$ to form isomer B of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$.

The $^{31}P\{^1H\}$ NMR spectrum of isomer A of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ exhibits five resonances of unequal relative intensities indicating a mixture of isomers. A matching of relative intensities suggests that resonances at −130.0, −118.0, and −32.8 ppm arise from one isomer (isomer A1 in Table IV) and that resonances at −133.6, −113.4, and −32.8 ppm arise from a second isomer (isomer A2 in Table IV) with the relative amounts of isomers A1 and A2 being about 65:35, respectively, and with the resonance at −32.8 ppm being common to both isomers. The pairs of resonances at −130.0 and −32.8 ppm in isomer A1 and at −133.6 and −32.6 ppm in isomer A2 contain a large splitting (237 Hz) indicative of two nonequivalent phosphorus atoms directly bonded to each other such as P^{AB} and P^B in V. The third resonances (−118.0 ppm in isomer A1 and −113.4 in isomer A2) contain no large splitting indicating that this phosphorus like P^{AA} in V is not directly bonded to either of the other phosphorus atoms. Thus the $^{31}P\{^1H\}$ NMR patterns of both forms of isomer A of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ indicate that exactly one of the phosphorus–phosphorus bonds of the triphosphaindane system II has been cleaved in its reaction with $Fe_3(CO)_{12}$ as depicted generally by structure V to form isomer A exactly as discussed above for isomer B of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$. The general chemical shift and coupling constant pattern for both forms of isomer A are very similar to each other and rather different from that of isomer B. This suggests that the structural difference between the two forms of isomer A is minor, possibly involving only a difference in stereochemistry, whereas the difference between either form of isomer A and isomer B of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ is major and involves a significant difference in the bonding of the $C_6H_4(PC_6H_5)_3$ unit to the system of three iron atoms. The two forms of isomer A may be isolable as separate species in the solid state since fractional crystallization of isomer A gives a yellow crystalline form (isomer A, yellow in Table II) from dilute solutions and a red crystalline form (isomer A, red in Table II) from concentrated solutions of distinctly different appearances. The red and yellow forms of isomer A have slightly different solid state infrared spectra (Nujol mulls) in the 1300–900-cm^{-1} region. The yellow form of isomer A retains solvent tenaciously and is photosensitive whereas the red form has neither of these two properties. However, in solution both the red and yellow modifications of isomer A give the same $^{31}P\{^1H\}$ NMR and infrared ν(CO) spectra indicative of a mixture of isomer A1 and A2 in the same relative quantities. This suggests that isomers A1 and A2 are in equilibrium with each other in solution, although the rate of equilibrium is slow relative to the NMR time scale since distinct resonances for two of the three phosphorus atoms in isomers A1 and A2 are observed. We have no definite proof that isomers A1 and A2 detected in solutions of isomer A by the $^{31}P\{^1H\}$ NMR spectrum correspond to the red and yellow forms of isomer A in the solid state although the evidence is highly suggestive.

A key clue to the structure of isomer A of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ appears to be the double doublet centered at −32.8 ppm in the $^{31}P\{^1H\}$ NMR spectrum which has a very similar chemical shift to the resonances centered at about −32.3 ppm in the free 1,2,3-triphenyl-1,2,3-triphosphaindane (II) assigned to the two essentially equivalent phosphorus atoms P^A in III. This suggests that isomer A of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ contains a C_6H_5P unit (P^{AB} in V) bonded directly to the *o*-phenylene ring and directly to another C_6H_5P unit but not to any iron atoms. This leaves only the two phosphorus atoms at the ends of the cleaved phosphorus–phosphorus bond in II (P^{AA} and P^B in V) for bonding to the $Fe_3(CO)_9$ unit. Each of these two phosphorus atoms can donate a total of three electrons to two iron atoms by acting as a bridging phosphido group completely analogous to the dialkylphosphido ligands in simple dialkylphosphido metal carbonyl derivatives.[5] An $Fe_3(CO)_9$ unit based on an iron triangle with three single iron–iron bonds as edges requires a total of six electrons from other ligands to attain the favored rare gas configuration implied by the diamagnetism. The two phosphorus atoms at the site of the cleaved phosphorus–phosphorus bond in II acting as bridging phosphido ligands (P^{AA} and P^B in V) contribute exactly the required six electrons for such an $Fe_3(CO)_9$ unit to attain the rare gas configuration. These considerations lead naturally to structure VI for isomer A of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ with the two forms (isomers A1 and A2) differing only in the orientation of the phenyl group on the uncomplexed phosphorus atom as indicated in structures VIa and VIb.

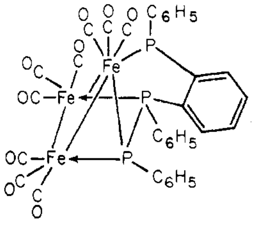


VIa



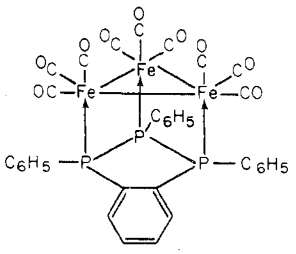
VIb

In isomer B of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ all of the $^{31}P\{^1H\}$ NMR resonances are shifted significantly downfield from those in the free 1,2,3-triphenyl-1,2,3-triphosphaindane (II) suggesting that all three phosphorus atoms are bonded to iron atoms. If the two phosphorus atoms at the ends of the cleaved phosphorus–phosphorus bond (i.e., the exterior phosphorus atoms or P^{AA} and P^B in V) are each bonded to the $Fe_3(CO)_9$ unit as bridging phosphido ligands and the third phosphorus atom (i.e., the interior phosphorus atom or P^{AB} in V) is bonded to the $Fe_3(CO)_9$ unit as a tertiary phosphine using its lone pair, then the unit from the singly cleaved $C_6H_4(PC_6H_5)_3$ ligand (V) can donate a total of eight electrons to the $Fe_3(CO)_9$ unit which would give an open chain $Fe_3(CO)_9$ unit with two iron–iron bonds the favored rare gas configuration. Alternatively, one of the lone pairs on the exterior phosphorus atoms can remain uncomplexed with a metal atom so that one of the exterior phosphorus atoms is bonded to the $Fe_3(CO)_9$ unit as a *terminal* phosphido ligand and the second exterior phosphorus atom as a bridging phosphido ligand with the interior phosphorus atom bonded as a tertiary phosphine. In this case the singly cleaved $C_6H_4(PC_6H_5)_3$ ligand V would donate a total of only six electrons to the $Fe_3(CO)_9$ unit which would give a closed triangular $Fe_3(CO)_9$ unit with three single iron–iron bonds the favored rare gas configuration for each iron atom. The latter alternative leading to structure VII for isomer B of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ appears most probable since the isolated exterior phosphorus atom (P^{AA} in V) has a significantly higher chemical shift (−74.4 ppm) in isomer B relative to isomer A (−113 to −118 ppm) of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ suggesting that this phosphorus atom retains an uncoordinated pair of electrons in isomer B.



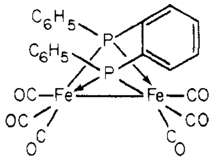
VII

Isomer C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ is perhaps the most unusual. The pattern of the large $^1J(PP)$ couplings (this time around 183 Hz) in the $^{31}P\{^1H\}$ NMR spectrum of this isomer corresponds to that of the free 1,2,3-triphenyl-1,2,3-triphosphaindane (II). The resonance corresponding to the central phosphorus atom of II (P^B in III) is shifted downfield by about 95 ppm in isomer C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ in accord with the usual effects of coordination of trivalent phosphorus atoms to transition metals.[20] However, the resonance corresponding to the remaining two phosphorus atoms of the ligand II (P^A in III) is shifted *upfield* by about 50 ppm in isomer C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ completely opposite to the usual downfield shift of trivalent phosphorus atoms upon coordination to transition metals. A triangular $Fe_3(CO)_9$ unit with three single iron–iron bonds requires six electrons to attain the favored rare gas electronic configuration. There is no precedent for such trimetallic iron carbonyl derivatives either not having the favored rare gas electronic configuration or having multiple iron–iron bonds in the iron triangle to reduce the number of external ligands required by the $Fe_3(CO)_9$ unit to attain the rare gas electronic configuration. These considerations suggest that the intact 1,2,3-triphenyl-1,2,3-triphosphaindane (II) must function as a six-electron donor in isomer C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$. This can only occur if each of the three phosphorus atoms in II coordinates like a tertiary phosphine by donating an electron pair to the $Fe_3(CO)_9$ unit thereby leading to structure VIII as the only reasonable alternative for isomer C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$. Unusual changes in bond angles are imposed by constraints in both the five-membered ring of the 1,2,3-triphosphaindane (II) and the iron triangle of the $Fe_3(CO)_9$ unit because of the need for the three phosphorus lone pairs of the ligand II to point inward to accommodate the iron triangle rather than outward as would be otherwise favored by the geometry of the ring system II and its constituent phosphorus atoms. These bond angle changes can account for the anomalous upfield coordination chemical shift of two of the three phosphorus atoms in going from the ligand II to isomer C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$. In order for the three lone pairs of the 1,2,3-triphenyl-1,2,3-triphosphaindane system II to point inward to bond to a single $Fe_3(CO)_9$ unit in structure VIII, the three P-phenyl groups of II must all point outward leading to the cis,cis isomer IIa as the ligand in isomer C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ in contrast to the trans,trans isomer IIc indicated by x-ray crystallography[18] for crystalline II and the cis,trans isomer IIb for II in solution suggested by our $^{31}P\{^1H\}$ NMR spectrum discussed above.

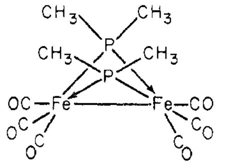


VIII

The remaining compound isolated from the reaction of 1,2,3-triphenyl-1,2,3-triphosphaindane (II) with $Fe_3(CO)_{12}$ is a yellow solid of stoichiometry $C_6H_4(PC_6H_5)_2Fe_2(CO)_6$ apparently formed by extrusion of the center C_6H_5P unit from the 1,2,3-triphosphaindane system II. Structure IX for this complex is supported by the close resemblance of the pattern of its infrared ν(CO) frequencies to those in the related complex $[(CH_3)_2PFe(CO)_3]_2$ (X)[3b] and by a single sharp singlet resonance in its $^{31}P\{^1H\}$ NMR spectrum consistent with the equivalence of both phosphorus atoms.



IX



X

Discussion

Studies on the reaction of 1,2,3-triphenyl-1,2,3-triphosphaindane (II) with $Fe_3(CO)_{12}$ at different temperatures (Table I) indicate that isomer A of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ is formed only under mild conditions and isomer C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ is formed only under relatively vigorous conditions (e.g., in boiling toluene but not in boiling benzene). Furthermore, the product $C_6H_4(PC_6H_5)_2Fe_2(CO)_6$ (IX), the only one involving extrusion of a C_6H_5P unit from II, is only produced under the most vigorous conditions short of complete decomposition (e.g., in boiling toluene for 24 hr). Any viable scheme for the formation of these products must be consistent with these observations.

The formation of $C_6H_4(PC_6H_5)_3[Fe(CO)_4]_2$ (IV) from $Fe_3(CO)_{12}$ and II involves simple complexation of the ligand II with two $Fe(CO)_4$ units without any bond cleavage or rearrangements of the five-numbered ring in II. The formation of isomers A, B, and C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ of structures VI, VII, and VIII, respectively, from this reaction is best rationalized if these isomers are formed in the sequence A → B → C, which is consistent with the yield data in Table I. Formation of isomer A from 1,2,3-triphenyl-1,2,3-triphosphaindane and $Fe_3(CO)_{12}$ involves interaction of the iron triangle with only the two phosphorus atoms at each end of the phosphorus–phosphorus bond of II undergoing cleavage since in structure VI for isomer A only these two phosphorus atoms are directly bonded to iron atoms. Conversion of isomer A to isomer B can be regarded as a simple shift of one of the iron–phosphorus bonds to the phosphorus atom not bonded to the iron atoms in isomer A. Conversion of isomer B to isomer C involves a migration from iron to phosphorus in which an iron–phosphorus bond becomes a phosphorus–phosphorus bond with regeneration of the 1,2,3-triphenyl-1,2,3-triphosphaindane ring system II but with the cis,cis stereochemistry IIa. The C_6H_5P extrusion product $C_6H_4(PC_6H_5)_2Fe_2(CO)_6$ (IX) can arise from fragmentation of VIII through cleavage of two iron–iron bonds and both phosphorus–phosphorus bonds with formation of two new iron–phosphorus bonds.

The interrelationships between these various structures with

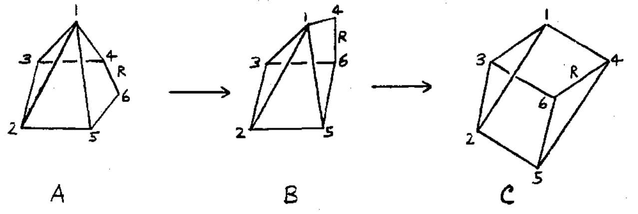


Figure 1. A topological representation of the interconversions of the three $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ isomers. The designation R along edge 46 indicates the location of the *o*-phenylene ring.

iron–phosphorus bonds can be visualized topologically as in Figure 1. Consider figures with six vertices corresponding to the three iron atoms (1, 2, and 3 in Figure 1) and the three phosphorus atoms (4, 5, and 6 in Figure 1) and with nine edges (designated by the numbers of the vertices which they join) corresponding to the three iron–iron bonds, a total of five iron–phosphorus and phosphorus–phosphorus bonds, and one *o*-phenylene bridge. Structure VI for isomer A of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ would correspond to a figure with one vertex (6 in A of Figure 1) of order 2, four vertices of order 3, and one vertex (1 in A of Figure 1) of order 4. This figure can be visualized more readily by performing a contraction in the graph-theoretical sense[21] making the *o*-phenylene bridge and the phosphorus–phosphorus bond into a single edge with deletion of the vertex of order 2 to give a figure topologically equivalent (i.e., homeomorphic[22]) to a square pyramid. Formation of isomer B from isomer A of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ involves moving edge 34 to become edge 36. The resulting figure for isomer B is isomorphic to the uncontracted figure for isomer A but the vertex of order 2 is now vertex 4. In view of the isomorphism of the figures representing isomers A and B of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$, the figure representing isomer B can also be contracted graph theoretically[21] to a figure topologically homeomorphic to a square pyramid, but this time by removal of vertex 4 rather than vertex 6. Conversion of isomer B to isomer C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ involves moving edge 15 to edge 45. The resulting figure corresponding to isomer C is topologically homeomorphic[22] to a trigonal prism with all vertices of order 3. The process of converting isomer A through isomer B to isomer C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ thus involves a chemically acceptable pathway (in terms of coordination numbers, electronic configurations, and stereochemistry) for equalizing the coordination of the iron and phosphorus atoms as represented topologically by going from a figure with vertices of orders two and four to a figure with only vertices of order three.

The apparent requirement of vigorous conditions for the formation of isomer C of $C_6H_4(PC_6H_5)_3Fe_3(CO)_9$ with an intact 1,2,3-triphosphaindane unit from the ligand II and $Fe_3(CO)_{12}$ apparently through a process such as that depicted in Figure 1 can be explained by the fact that the cis,cis isomer IIa of the ligand is required for isomer C. This cis,cis isomer IIa of the 1,2,3-triphosphaindane is too unfavorable sterically to be formed by direct isomerization of the cis,trans or trans,trans isomers of II but has to be constructed through forming a template by phosphorus–phosphorus bond rupture and interaction with the metal triangle followed by regeneration of the phosphorus–phosphorus bond after the coordination to the metal triangle has been made suitable for holding the phenyl groups in the 1,2,3-triphenyl-1,2,3-triphosphaindane system II in the cis,cis configuration IIa. Processes such as those depicted topologically in Figure 1 may be relevant to catalysis involving metal clusters including the free metals themselves, although the details will naturally depend on the exact type of process being catalyzed.

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Registry No. $C_6H_4(PPh)_3$, 57194-41-9; $C_6H_4(PPh)_3[Fe(CO)_4]_2$, 57139-05-6; $C_6H_4(PPh)_3Fe_3(CO)_9$ (A), 57173-83-8; $C_6H_4(PPh)_3Fe_3(CO)_9$ (B), 57139-06-7; $C_6H_4(PPh)_3Fe_3(CO)_9$ (C), 57139-07-8; $C_6H_4(PPh)_2Fe_2(CO)_6$, 57139-08-9; $Fe_3(CO)_{12}$, 17685-52-8; $Fe_2(CO)_9$, 15321-51-4; ^{31}P, 7723-14-0.

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