

## SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF DINUCLEAR CYCLOPENTADIENYLIRON(II) COMPLEXES WITH TRITERTIARY PHOSPHINES AS BRIDGING LIGANDS

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### Summary

Cationic dinuclear cyclopentadienyl complexes containing tripod polytertiary phosphines as bridging ligands have been synthesized. The complexes  $[(C_5H_5)Fe(CO)I-L-Fe(C_5H_5)]Y$  ( $L =$  tris(2-diphenylphosphinoethyl)amine,  $np_3$ ; or tris(2-diphenylphosphinoethyl)phosphine,  $pp_3$ ;  $Y = PF_6^-$ ) were obtained by reaction of  $(C_5H_5)Fe(CO)_2I$  with the appropriate phosphorus ligands. The structure of the  $np_3$  derivative was determined by X-ray diffraction. The crystals are monoclinic, space group  $P2_1/n$  with cell dimensions  $a$  16.393(5),  $b$  22.317(6),  $c$  15.345(5) Å,  $\beta$  113.03(4)°,  $D_c$  1.55 g cm<sup>-3</sup> for  $Z = 4$ . The structure was solved by three dimensional Patterson and Fourier syntheses and refined by least-squares techniques to a final conventional  $R$  factor of 0.074. The structure consists of dinuclear  $[(C_5H_5)Fe(CO)I-np_3-Fe(C_5H_5)]^+$  cations and  $PF_6^-$  anions. The nitrogen and two phosphorus atoms of the  $np_3$  ligand are bound to an cyclopentadienyliron group, while the other phosphorus atom of the ligand is bound to a cyclopentadienyliron-carbon monoxide-iodide moiety.

### Introduction

Substitution reactions involving cyclopentadienylmetal carbonyl halides and tertiary phosphines have been extensively investigated [1]. The geometry of the complexes obtained depends on the metal and the number of donor atoms in the ligands [2–4]. In particular, cyclopentadienyliron halides,  $(C_5H_5)Fe(CO)_2X$ , ( $X =$  halogen), and triarylphosphines react to give compounds of formula  $[(C_5H_5)Fe(CO)_nPR_3]Y$  ( $n = 1, 2, Y =$  halogen or  $PF_6^-$ ) [3]. When the reaction is carried out with the tridentate 1,1,1-tris(diphenylphosphinomethyl)ethane,  $p_3$ , or the tetradentate tris(2-diphenylphosphinoethyl)phosphine,  $pp_3$ , complexes are obtained in which the central ion reaches the 18 electrons configuration by

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coordinating the three phosphorus atoms of  $p_3$  or two phosphorus atoms of the tripod  $pp_3$  ligand [2,5].

Treatment of  $(C_5H_5)Fe(CO)_2I$  with tris(2-diphenylphosphinoethyl)amine,  $np_3$  gives the cationic dinuclear complex  $[(C_5H_5)Fe(CO)I-np_3-Fe(C_5H_5)]PF_6$ , in which the ligand  $np_3$  bridges two iron(II) moieties. An isomorphous compound is obtained using the ligand  $pp_3$ . The complexes have been characterized by standard physical methods, and a complete X-ray structural analysis has been carried out for the  $np_3$  derivative.

## Experimental

Solvents were of reagent grade quality and were used without further purification. The ligand  $np_3$  was prepared as previously reported [6];  $pp_3$  and  $(C_5H_5)Fe(CO)_2I$  were purchased from the Pressure Chemical Company and Strem Chemical Inc., respectively.

### *Preparation of $[(C_5H_5)Fe(CO)I-np_3-Fe(C_5H_5)]PF_6$*

A suspension of  $(C_5H_5)Fe(CO)_2I$  (1 mmol) and the ligand  $np_3$  (0.5 mmol) in benzene (50 ml) was exposed to ultraviolet irradiation for 45 min. After filtration the solvent was removed in vacuo at room temperature. The residual green oil was dissolved in methylene chloride (30 ml) a solution of tetrabutylammonium hexafluorophosphate (1 mmol) in methanol (15 ml) was added. The solution was refluxed for 1 h and concentrated under nitrogen. Brown crystals separated and were filtered off, washed with methanol then with light petroleum, and dried. Anal. Found: C, 53.2; H, 4.5; Fe, 9.1; N, 1.1; P, 10.5.  $C_{53}H_{52}F_6Fe_2INOP_4$  calcd.: C, 53.3; H, 4.4; Fe, 9.3; N, 1.2; P, 10.4%.

### *Preparation of $[(C_5H_5)Fe(CO)I-pp_3-Fe(C_5H_5)]PF_6$*

This complex was prepared as brown crystals by the method described for the  $np_3$  derivative. Anal. Found: C, 52.2; H, 4.4; Fe, 9.0; P, 12.8.  $C_{53}H_{52}F_6Fe_2IOP_5$  calcd.: C, 52.5; H, 4.3; Fe, 9.2; P, 12.9%.

### *Physical measurements*

Magnetic, conductometric and spectrophotometric measurements (both visible and infrared) were carried out as previously described [7]. NMR spectra were recorded with methylene chloride- $d_2$  solutions; proton spectra were recorded at 90 MHz on a Varian EM390 Spectrometer equipped with a variable temperature probe; phosphorus-31 spectra were recorded on a Varian CFT 20 Spectrometer at 32.19 MHz in the Fourier transform mode with proton decoupling. Chemical shifts are reported in ppm with positive values to high field of tetramethylsilane for  $^1H$  spectra and 85% phosphoric acid for  $^{31}P$  spectra. Coordination chemical shifts are given in ppm relative to the signal from the corresponding phosphorus atom in the free ligand.

### *Crystal data and data collection*

The crystal used for data collection was a parallelepiped of dimensions  $0.2 \times 0.3 \times 0.5$  mm. The crystals are monoclinic and belong to the space group  $P2_1/n$ , with  $4[(C_5H_5)Fe(CO)I-np_3-Fe(C_5H_5)]PF_6$  formulas in the unit cell, which has

the following dimensions:  $a$  16.393(5),  $b$  22.317(6),  $c$  15.345(5) Å,  $\beta$  113.03(4)°.

Intensity data were collected on an automatic computer-controlled diffractometer Philips PW 1100 equipped with a graphite monochromator, using Mo- $K_{\alpha}$  radiation. All reflections with  $6^{\circ} \leq 2\theta \leq 40^{\circ}$  were measured using the  $\omega - 2\theta$  scan technique with a scan speed of  $0.08^{\circ}/s$  in a range of  $0.8^{\circ}$  across the peak. Background times were taken as equal to half the scan time on each side of the peak. Three standard reflections were measured every 120 minutes during data collection, but no significant trend was noticed.

The intensity data were corrected for Lorentz and polarization effects; the standard deviation  $\sigma(I)$  was estimated as described elsewhere [8], with an instability factor equal to 0.03. A reflection was considered unobserved if the net intensity  $I$  was  $< 3\sigma(I)$ . From 5170 total reflections, 1878 had intensity  $\geq 3\sigma(I)$ . An absorption correction,  $\mu(\text{Mo-}K_{\alpha})$   $13.30 \text{ cm}^{-1}$ , was made by a numerical method: transmission factors varied between 0.73 and 0.82. Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Waber's lists [9], and those for hydrogen atoms from Stewart et al. [10]. Corrections for anomalous dispersion effects for iodine, iron and phosphorus atoms were made in the refinement stage [11].

#### *Structure solution and refinement*

The position of the two iron and iodine atoms were obtained from a Patterson synthesis. Except for the atoms of the carbon monoxide, the other atoms were located from successive  $F_0$  Fourier maps. Near the positions expected for the atoms of the carbon monoxide, the  $F_0$  map, as well as the  $\Delta F$  map, shows only one maximum, which has a height intermediate between that of a phosphorus atom and that of a carbon atom. This maximum is about 2.6 Å from the metal. Since the presence of the carbon monoxide appears evident from the strong  $\nu(\text{CO})$  band, it has been assumed that this maximum of electron density is due to a statistical disorder between the iodine and the carbon monoxide molecule linked to the same iron atom. Because of this the carbon and oxygen atoms of the carbon monoxide are covered by the heavier iodine atom which occupies an intermediate position between the carbon and oxygen atoms.

The structure was refined by a full-matrix least-squares program [12]. The minimized function is  $\sum w(|F_0| - |F_C|)^2$ , where  $w$  is the weight assigned to the  $F_0$  values according to the expression  $w = 1/\sigma(F_0)^2$ . The atoms of the carbon monoxide were introduced in calculated positions on the Fe—I line, with a Fe—C distance of 1.75 Å and a C—O distance of 1.15 Å. These atoms were not refined. Isotopic temperature factors  $B$  equal to  $4 \text{ \AA}^2$  were assigned to these atoms. Population parameters for these atoms were assigned on the basis of the population parameters of the iodine atoms, which were refined to a final value of 0.8 and 0.2. The carbon atoms of the phenyl groups were refined using rigid-body models for the phenyl rings. The hydride atoms were introduced in the calculated positions (C—H distance of 0.95 Å), with an isotropic thermal factor  $B_{\text{H}} = B_{\text{C attached}} + 1$ , and were not refined. Anisotropic temperature factors were used for iodine, iron, phosphorus and fluorine atoms; isotropic temperature factors were used for the other atoms. The final refinement gave an  $R$  value of 0.074, whereas  $R_w$ , defined as  $[\sum w(|F_0| - |F_C|)^2 / \sum w F_0^2]^{1/2}$ , was 0.079. A final  $\Delta F$  Fourier did not show remarkable features. The final positional

TABLE 1  
 ATOMIC <sup>a</sup> PARAMETERS FOR THE STRUCTURE OF  $[(C_5H_5)Fe(CO)]-m\pi_3-Fe(C_5H_5)PF_6$  (all quantities  $\times 10^4$ )

Atom	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
I(1) <sup>b</sup>	1481(2)	4397(2)	267(2)	957(26)	1749(36)	526(19)	-401(25)	259(18)	-576(22)
I(2) <sup>c</sup>	3254(14)	3849(7)	2394(12)	3300(236)	1120(132)	2095(174)	119(140)	2166(181)	278(119)
Fe(1)	2842(3)	4853(2)	1641(3)	693(34)	884(40)	394(27)	-150(30)	235(25)	-90(27)
Fe(2)	1016(2)	3107(2)	3926(2)	435(28)	561(32)	281(24)	74(25)	125(22)	114(22)
P(1)	2036(5)	5196(4)	2412(4)	411(51)	663(62)	111(42)	-116(47)	47(39)	49(41)
P(2)	83(5)	3382(4)	4583(5)	520(57)	614(64)	337(49)	56(48)	195(45)	155(44)
P(3)	41(5)	2605(3)	2744(5)	476(56)	382(58)	363(45)	-26(46)	82(43)	95(42)
P(4)	6692(8)	3981(5)	1699(6)	966(100)	596(85)	417(68)	183(73)	121(67)	-141(58)
F(1)	6148(18)	3847(11)	674(14)	2791(309)	1867(238)	435(157)	-319(212)	-472(177)	-412(153)
F(2)	6930(19)	3345(12)	1859(13)	2757(359)	1471(254)	649(160)	603(245)	347(191)	-41(163)
F(3)	7245(17)	4098(11)	2748(13)	2205(290)	2405(294)	781(154)	-336(221)	-58(171)	-628(170)
F(4)	5867(15)	3898(16)	1922(19)	972(194)	3743(481)	1842(298)	-319(237)	701(212)	173(290)
F(5)	6489(19)	4605(12)	1518(17)	2560(334)	1043(246)	1761(249)	59(232)	183(223)	-217(193)
F(6)	7494(16)	4071(13)	1510(16)	1281(219)	2856(387)	1169(207)	621(224)	456(180)	713(211)

F. rel. scale factor 61470

<sup>a</sup> The form of the thermal ellipsoid is  $\exp[-2\pi^2(U_{11}h^2a^2 + U_{22}k^2b^2 + U_{33}l^2c^2 + 2U_{12}hka^*b^* + \dots)]$ . <sup>b</sup> Population parameters of 0.8. <sup>c</sup> Population parameter of 0.2.

TABLE 2

ATOMIC PARAMETERS FOR  $[(C_5H_5)Fe(CO)I-np_3-Fe(C_5H_5)]PF_6$  (All quantities  $\times 10^4$ )

Atom	x	y	z	U (Å <sup>2</sup> )
N	504(13)	3879(9)	2987(13)	391(59)
C(1)	3932(25)	4818(16)	1262(27)	1330(138)
C(2)	4155(22)	5104(16)	2175(24)	1017(117)
C(3)	3636(20)	5622(14)	2047(21)	750(99)
C(4)	3060(18)	5665(14)	1082(20)	834(97)
C(5)	3299(22)	5197(16)	603(23)	1121(116)
C(6)	1230(15)	4198(10)	2852(15)	426(72)
C(7)	1040(15)	4798(11)	2317(15)	463(72)
C(8)	85(15)	4324(11)	3421(15)	509(73)
C(9)	-501(16)	4003(11)	3842(16)	585(78)
C(10)	-184(15)	3714(10)	2005(15)	461(71)
C(11)	-750(15)	3169(11)	2019(16)	481(76)
C(12)	2013(15)	2487(11)	3996(16)	488(77)
C(13)	2330(15)	3055(11)	4033(16)	469(74)
C(14)	2319(16)	3373(11)	4827(18)	591(83)
C(15)	1983(16)	2959(12)	5271(17)	433(78)
C(16)	1795(16)	2433(12)	4784(18)	623(83)

and thermal parameters are listed in Tables 1-4. Tables of structure factors may be obtained from the authors.

### Results and discussion

The new complexes described,  $[(C_5H_5)Fe(CO)I-L-Fe(C_5H_5)]Y$  with  $L = np_3$  or  $pp_3$ , were obtained by reaction of  $(C_5H_5)Fe(CO)_2I$  and the ligand  $np_3$  or  $pp_3$  in benzene; the  $pp_3$  derivative is obtained in low yield owing to the formation of a yellow precipitate, probably the known complex  $[(C_5H_5)Fe-pp_3]I$  [5].

The complexes are fairly air stable and behave as 1/1 electrolytes in nitroethane. They are diamagnetic and isomorphous in the solid state. The infrared spectra in Nujol mulls show an intense band at ca.  $1960\text{ cm}^{-1}$  characteristic of a terminal CO stretching band. The electronic spectra in the solid state show a band at 1.78 and 1.69 and a shoulder at 1.10 and  $1.07\text{ Å}^{-1}$ , respectively, for the

TABLE 3

FINAL LEAST SQUARES PARAMETERS FOR  $[(C_5H_5)Fe(CO)I-np_3-Fe(C_5H_5)]PF_6$  GROUPS <sup>a</sup>

Group	x'	y'	z'	$\theta$	$\phi$	$\psi$
1	0.1306(7)	0.5418(6)	0.1796(9)	2.156(13)	0.384(15)	1.484(14)
2	0.2938(8)	0.5223(5)	0.4575(9)	1.584(13)	1.622(13)	-2.688(18)
3	-0.1244(9)	0.2548(6)	0.4862(7)	0.482(11)	2.805(21)	-0.369(20)
4	0.0830(7)	0.4028(5)	0.6521(8)	1.997(15)	1.214(14)	-0.835(12)
5	-0.0988(8)	0.1608(6)	0.3103(7)	2.669(10)	-2.727(18)	2.635(19)
6	0.0538(8)	0.2084(5)	0.1170(8)	2.250(10)	-1.651(13)	-1.154(12)

<sup>a</sup>  $x'$ ,  $y'$ ,  $z'$  (fractional coordinates) define the origin of the working system of the group. The definition is used for Euler angles:  $\theta$ ,  $\phi$ ,  $\psi$  (radians) [19].

TABLE 4

THERMAL AND DERIVED POSITIONAL PARAMETERS OF GROUP ATOMS (all quantities  $\times 10^4$ )

Atom		x	y	z	$U (\text{\AA}^2)$
C(1)	1	1611(12)	5934(7)	2060(14)	419(82)
C(2)	1	949(12)	6005(7)	1159(14)	714(93)
C(3)	1	593(12)	6570(7)	852(14)	739(97)
C(4)	1	899(12)	7064(7)	1444(14)	979(113)
C(5)	1	1561(12)	6993(7)	2344(14)	964(108)
C(6)	1	1917(12)	6428(7)	2652(14)	706(91)
C(1)	2	2599(12)	5242(8)	3731(9)	509(84)
C(2)	2	2152(12)	5467(8)	4268(9)	706(94)
C(3)	2	2548(12)	5445(8)	5253(9)	627(86)
C(4)	2	3390(12)	5199(8)	5700(9)	1048(106)
C(5)	2	3836(12)	4974(8)	5163(9)	816(97)
C(6)	2	3440(12)	4995(8)	4179(9)	800(95)
C(1)	3	-727(13)	2876(8)	4732(11)	461(84)
C(2)	3	-1617(13)	3037(8)	4419(11)	760(97)
C(3)	3	-2219(13)	2655(8)	4570(11)	1000(110)
C(4)	3	-1933(13)	2111(8)	5034(11)	864(106)
C(5)	3	-1043(13)	1951(8)	5348(11)	785(97)
C(6)	3	-440(13)	2333(8)	5197(11)	672(92)
C(1)	4	604(10)	3751(7)	5801(10)	616(85)
C(2)	4	1178(10)	4235(7)	5949(10)	748(96)
C(3)	4	1442(10)	4559(7)	6790(10)	828(98)
C(4)	4	1132(10)	4398(7)	7482(10)	793(92)
C(5)	4	558(10)	3914(7)	7334(10)	704(88)
C(6)	4	294(10)	3590(7)	6493(10)	857(96)
C(1)	5	-589(13)	2013(8)	2948(10)	458(85)
C(2)	5	-1502(13)	2056(8)	2683(10)	568(82)
C(3)	5	-1967(13)	1583(8)	2864(10)	766(90)
C(4)	5	-1519(13)	1067(8)	3310(10)	777(97)
C(5)	5	-607(13)	1025(8)	3575(10)	691(94)
C(6)	5	-142(13)	1498(8)	3394(10)	695(88)
C(1)	6	385(9)	2259(8)	1825(10)	462(81)
C(2)	6	1038(9)	2536(8)	1598(10)	480(76)
C(3)	6	1216(9)	2332(8)	834(10)	627(87)
C(4)	6	742(9)	1851(8)	296(10)	861(111)
C(5)	6	90(9)	1573(8)	522(10)	987(112)
C(6)	6	-89(9)	1777(8)	1287(10)	823(101)

$np_3$  and  $pp_3$  derivative; these spectra are typical of complexes in which the metal atom is in low spin state with an 18 electron configuration.

A complete X-ray structural analysis has been carried out on the  $np_3$  derivative. The structure consists of cations  $[(C_5H_5)Fe(CO)I-np_3-Fe(C_5H_5)]^+$  and of  $PF_6^-$  anions. A perspective view of the cation is shown in Fig. 1. The Fe(1) atom is surrounded by an iodine atom, a carbon atom of a CO molecule, a phosphorus atom of the  $np_3$  ligand, and a  $C_5H_5$  ring, whereas the Fe(2) atom is surrounded by the other donor atoms of the ligand (two phosphorus and a nitrogen) and by a  $C_5H_5$  ring. Although the two iron atoms are not equivalent they are both in a distorted tetrahedral environment. In agreement with a previous observation [13], the tetrahedral geometry can be regarded as derived from an octahedral arrangement in which three facial points collapse to one point. The observed values of the angles at Fe(1) associated with P(1), I, and at Fe(2) associated with P(2), P(3), N, which are all close to  $90^\circ$ , support this

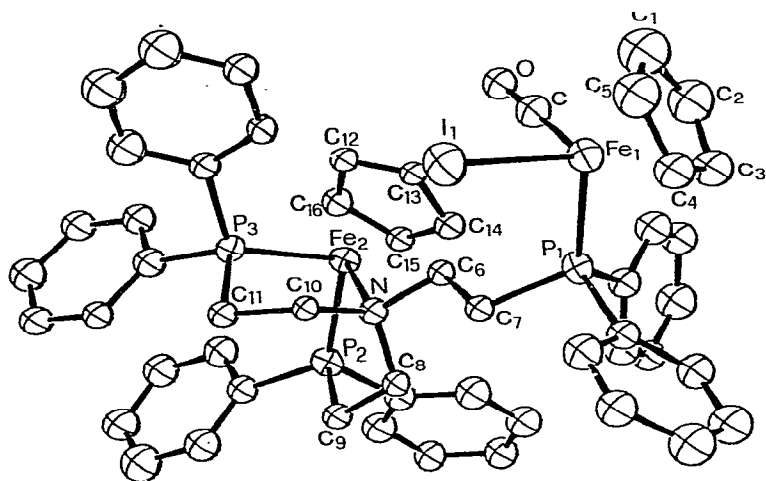


Fig. 1. Perspective view of the complex cation  $[(C_5H_5)Fe(CO)I-np_3-Fe(C_5H_5)]^+$ . ORTEP diagram showing 30% probability ellipsoids.

TABLE 5

SELECTED BOND LENGTHS (Å) AND ANGLES (deg)

Fe(1)—I(1)	2.603(5)	C(10)—C(11)	1.53(4)
Fe(1)—P(1)	2.228(10)	P(1)—C(7)	1.81(3)
Fe(1)—C(1)	2.09(5)	P(2)—C(9)	1.81(2)
Fe(1)—C(2)	2.06(3)	P(3)—C(11)	1.84(2)
Fe(1)—C(3)	2.10(3)	C(1)—C(2)	1.45(5)
Fe(1)—C(4)	2.09(3)	C(1)—C(5)	1.41(5)
Fe(1)—C(5)	2.15(4)	C(2)—C(3)	1.40(5)
Fe(2)—P(2)	2.223(10)	C(3)—C(4)	1.41(4)
Fe(2)—P(3)	2.199(7)	C(4)—C(5)	1.42(5)
Fe(2)—N	2.19(2)	C(12)—C(13)	1.36(4)
Fe(2)—C(12)	2.11(3)	C(12)—C(16)	1.39(4)
Fe(2)—C(13)	2.10(3)	C(13)—C(14)	1.42(4)
Fe(2)—C(14)	2.12(2)	C(14)—C(15)	1.38(4)
Fe(2)—C(15)	2.08(2)	C(15)—C(16)	1.36(4)
Fe(2)—C(16)	2.08(2)	P(4)—F(1)	1.50(2)
N—C(6)	1.47(3)	P(4)—F(2)	1.47(3)
N—C(8)	1.50(3)	P(4)—F(3)	1.53(2)
N—C(10)	1.53(2)	P(4)—F(4)	1.53(3)
C(6)—C(7)	1.54(3)	P(4)—F(5)	1.43(3)
C(8)—C(9)	1.53(4)	P(4)—F(6)	1.47(3)
I(1)—Fe(1)—P(1)	93.8(2)	P(2)—C(9)—C(8)	111.1(17)
P(2)—Fe(2)—P(3)	96.1(3)	N—C(10)—C(11)	113.1(19)
P(2)—Fe(2)—N	85.8(7)	P(3)—C(11)—C(10)	105.3(15)
P(3)—Fe(2)—N	83.7(5)	C(2)—C(1)—C(5)	105.4(32)
Fe(2)—N—C(6)	110.5(13)	C(1)—C(2)—C(3)	108.5(26)
Fe(2)—N—C(8)	110.7(14)	C(2)—C(3)—C(4)	108.8(29)
Fe(2)—N—C(10)	113.7(13)	C(3)—C(4)—C(5)	106.6(26)
C(6)—N—C(8)	106.1(18)	C(1)—C(5)—C(4)	110.1(30)
C(6)—N—C(10)	107.6(18)	C(13)—C(12)—C(16)	105.6(23)
C(8)—N—C(10)	107.8(16)	C(12)—C(13)—C(14)	111.6(25)
N—C(6)—C(7)	119.5(19)	C(13)—C(14)—C(15)	103.3(22)
P(1)—C(7)—C(6)	113.3(15)	C(14)—C(15)—C(16)	110.7(26)
N—C(8)—C(9)	110.4(20)	C(12)—C(16)—C(15)	108.7(25)

view (Table 5). This situation is usually observed for coordination polyhedra of the general type  $(C_5H_5)ML^1L^2L^3$  [13]. It has been previously pointed out that the Fe—(ring centroid) distances fall into two groups: ferrocene derivatives have Fe—(ring centroid) distances of about 1.65 Å [14,15], while those of  $(C_5H_5)FeL^1L^2L^3$  show longer distances, which vary in the range 1.70–1.75 Å depending on the nature of the  $L^1$ ,  $L^2$  and  $L^3$  ligands [16,13,17]. The two Fe—(ring centroid) distances for the complex here reported fall within the latter group, and are 1.717 Å for Fe(1) and 1.741 Å for Fe(2). This difference, though small, may be due to the differing abilities of donor atoms to compete for the iron electrons. As a consequence the C(1)—C(5) ring has an average C—C distance (1.418 Å) larger than that found for the C(12)—C(16) ring (1.382 Å).

The distance Fe(2)—N, 2.19(2) Å, Table 5, which is comparable to the Fe—P distances, is significantly longer than that in other  $np_3$  complexes [18]. Furthermore the N—C(6)—C(7)—P(1) chain is considerably stretched, the angles around C(6) and C(7) being 119.5(19) and 113.3(15)°, respectively. This stretching may be due to the steric constraint on the ligand when bound to two iron atoms. (This is the first case in which the  $np_3$  ligand acts as a bridging molecule between two metal ions.)

The  $np_3$  derivative retains the same geometry in solution: the electronic spectrum in nitroethane solution is the same as that in the solid state (a band at 1.77 ( $\epsilon$  430), a shoulder at 1.10 Å<sup>-1</sup>); <sup>1</sup>H and <sup>31</sup>P nuclear magnetic resonance spectra are in agreement with the structure described above. The <sup>1</sup>H spectrum shows a doublet ( $\delta$  4.44 ppm,  $J(H-P)$  1.6 Hz) and a triplet ( $\delta$  3.97 ppm,  $J(H-P)$  2 Hz) with a relative intensity 1/1 due to the cyclopentadienyl protons bound to the Fe(1) and Fe(2), respectively. The <sup>31</sup>P spectrum shows two signals due to the phosphorous atoms of the ligands in a ratio 1/2 at  $\delta$  -60.33 and -74.25 ppm, with coordination chemical shifts of -80.63 and -94.55 ppm. The green solutions of the  $pp_3$  derivative in nitroethane or 1,2-dichloroethane, on the other hand, show electronic spectra (two bands at 1.64 ( $\epsilon$  = 60) and at 2.27 Å<sup>-1</sup> ( $\epsilon$  = 110)) which are quite different from that of the solid state. <sup>1</sup>H and <sup>31</sup>P spectra, recorded at several temperatures, did not permit identification of the species present in solution.

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