THE PREPARATION AND CRYSTAL STRUCTURE OF $Fe_3(CO)_9(\mu_3\text{-PPh})_2$

STEPHEN L. COOK, JOHN EVANS *, LESLIE R. GRAY and MICHAEL WEBSTER *

Department of Chemistry, The University, Southampton SO9 5NH (Great Britain)

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Summary

$Fe_3(CO)_9(\mu_3\text{-PPh})_2$ has been isolated from the reaction between $Fe_3(CO)_{12}$ and $PhPH_2$ in refluxing toluene. X-ray diffraction ($R = 0.0619$) shows an open chain of $Fe(CO)_3$ groups (average Fe—Fe—Fe angle 81.4°) capped by μ_3-PPh groups on both faces. The average Fe—Fe and Fe—P distances were 2.717 and 2.218 Å respectively.

Introduction

Dodecacarbonyltriiron has been reported to react with $PPhH_2$ to afford $(\mu\text{-H})_2Fe_3(CO)_9(\mu_3\text{-PPh})$ (I) as the sole product [1]. We were therefore interested in this reaction as a possible basis of anchoring a triiron cluster to a functionalised oxide support since we have found that bridging anchoring ligands enhance the stability of tethered clusters [2]. We report the isolation of $Fe_3(CO)_9(\mu_3\text{-PPh})_2$ (II) from this reaction; complex II has been recently reported as one of three cluster products from the reaction between $Fe_2(CO)_6(PHPh)_2$ and $Fe_3(CO)_{12}$ [3].

Experimental

$Fe_3(CO)_{12}$ [4] and $PPhH_2$ [5] were both prepared according to published procedures.

IR, NMR and mass spectra were recorded on a Perkin—Elmer 580B, Varian XL-100 and AEI MS12 respectively.

Reaction of $Fe_3(CO)_{12}$ and $PhPH_2$

$PhPH_2$ (1.1 g, 10 mmol) was added to a degassed solution of $Fe_3(CO)_{12}$ (5 g, 9.9 mmol) in sodium dried toluene (150 cm³) under nitrogen. The mixture was refluxed for 16 h, during which time the solution colour changed from dark

green to dark red. After it was cooled to room temperature, the solution was filtered through silica gel and evaporated to dryness. The residue was extracted with 40/60 petroleum ether (250 cm^3), filtered through silica gel and the solvent removed to afford a dark red oil which was dried in vacuo. The infrared spectrum of the product mixture (in cyclohexane: 2092m, 2058s, 2042s, 2031s, 2021s, 2016wsh, 2006s, 2000wsh, 1993w, 1988w, 1987wsh and 1981w cm^{-1}) indicated a mixture of I and another product II. The product was purified by TLC on silica gel plates using 40/60 petroleum ether (95%)/CH$_2$Cl$_2$ (5%) as solvent. Four bands were obtained and the product, Fe$_3$(CO)$_9$(PPh)$_2$ (II), was extracted from the major (red) band. Yield ~20%.

IR (cyclohexane): 2042vs, 2021s, 2006m, 1993w and 1982w cm^{-1}. Mass spectrum (70 eV) shows the molecular ion (Fe$_3$(CO)$_9$(PPh)$_2$$^+$) at 636 amu and nine losses of CO to the Fe$_3$(PPh)$_2$$^+$ ion (384 amu) and another prominent Fe$_3$ isotope pattern around 306 amu (Fe$_3$P(PPh)$^+$). ^{1}H NMR: (CDCl$_3$) δ 7.5(m). {^{1}H} ^{13}C NMR (CDCl$_3$): δ 213.2(s,CO), 207.3(br,CO), 137.4(s,C$_{ipso}$) 132.3("t", J(P$_1$C) + J(P$_2$C) ~7 Hz, C$_{ortho}$), 131.7(s,C$_{para}$) and 129.0("t",J(P$_1$C) + J(P$_2$C) 10 Hz, C$_{meta}$).

X-ray crystallography: data collection and structure determination

Air stable red needle crystals of Fe$_3$(CO)$_9$(PPh)$_2$ were obtained from n-pentane solution and subjected to preliminary X-ray photographic examination. The compound is triclinic, a 11.446(8), b 14.191(4), c 15.586(7) Å, α 83.97(3), β 86.47(5), γ 82.63(5)°, U 2493.9 Å^3. There are 4 molecules of C$_{21}$H$_{10}$Fe$_3$O$_9$P$_2$, MWt = 635.79 per unit cell, D_c 1.693, D_0 1.6(1) g cm^{-3}, F(000) 1264, μ(Mo-K_α) 18.93 cm^{-1} and the structure was solved in the space group $P\bar{1}$ (No 2).

Crystal data were collected on a CAD-4 diffractometer using graphite monochromated Mo-K_α radiation (λ 0.7107 Å) from a room temperature crystal (0.30 × 0.025 × ~0.1 mm). The cell dimensions were determined from 25 accurately centred reflections. Three check reflections showed no deterioration during the experiment and a total of 6929 reflections were recorded (1.5 $\leqslant \theta \leqslant$ 23°). The small crystal scattered weakly and there were a number of reflections with F_0 = 0.0(1621). Of the remaining non-zero reflections those with $F <$ 3σ(F) were eliminated leaving 2902 reflections which were used in the structure determination and refinement. Direct methods located two Fe$_3$P$_2$ clusters and subsequent structure factor and electron density synthesis located the remaining non-hydrogen atoms.

The crystal was an irregular fragment and since no suitable reflections were available for an empirical ψ-scan absorption correction the technique described by Walker [6] was applied. Least squares refinement with isotropic atoms, phenyl rings as rigid groups and hydrogen atoms in calculated positions gave R = 0.102 and at this stage the absorption correction was applied. Subsequent least squares refinement introducing anisotropic Fe and P atoms and an empirical weighting scheme (W = 1/(σ^2(F) + AF_0^2), A = 0.0006) gave a converged R = 0.0619 (R_w = 0.0590). A final difference electron density synthesis showed —0.77 < electron density < 1.04 eÅ^{-3}. The number of refined parameters is 284 and the ratio reflections/parameters is 10.22. All calculations were performed on an ICL2970 computer using primarily the programs SHELX [7],

PLUTO [8], and DIFABS [6]. Atomic scattering factors for neutral atoms and anomalous dispersion corrections were taken from the SHELX package (P,O,C,H) and from International Tables for X-ray crystallography (Fe) [9].

Results and discussion

The formulation of complex II is entirely consistent with the observed mass and NMR spectra. Assignments of the aromatic ^{13}C resonances were based on those of other PPh fragments [10]. The ^{13}CO region of the NMR spectrum apparently shows parallel behaviour to that observed for $Os_3(CO)_9(PEt)(C_6H_4)$ [11]. So the sharp peak at δ 213.2 is assigned to a rotating $Fe(CO)_3$ group and the broader resonance at δ 207.2 due to intermediate exchange behaviour involving more restricted localised rotation of the two outer $Fe(CO)_3$ moieties (vide infra). It is unclear why II was not observed by Huttner et al. [1]. Some product differences have been reported in the products obtained from the reaction between $Ru_3(CO)_{12}$ and $PPhH_2$, under varying conditions. Whilst trinuclear products were obtained after 40 min in refluxing cyclohexane [12], $Ru_4(PPh)_2$-$(CO)_{11}$ (III) and $Ru_5(CO)_{15}(PPh)$ (IV) were obtained additionally in refluxing toluene [13]. We have detected III after 1 h in refluxing cyclohexane, but production of IV requires longer reaction times, e.g. 16 h. Complex II was first prepared in refluxing decalin [14].

The molecular structure of $Fe_3(CO)_9(PPh)_2$ was determined by X-ray diffraction. The final atomic coordinates and temperature factors are shown in Tables 1 and 2 and tables of observed and calculated structure factors are available (from J.E.) on request. The crystal contains two crystallographically independent molecules (A and B) which have nearly identical geometry. Figure 1 shows molecule A and in Fig. 2 the detailed molecular packing is illustrated. In Table 3 are given selected bond lengths for the two molecules.

The molecule consists of a bent chain of iron atoms (average Fe—Fe—Fe angle 81.4°C) with two μ_3-PPh groups. This may be described as a *nido* octahedron, in accordance with having 7 skeletal electron pairs [15] and similar to $Fe_3(CO)_9Se_2$ (V) [16] and $Fe_3(CO)_9S_2$ (VI) [17]. $Fe_3(CO)_9As_2$ (VII), with six skeletal electron pairs, presents a *closo*-trigonal bipyramid with three intact Fe—Fe bonds (average 2.623 Å) [18]. Extended Hückel MO calculations on VII found the lowest unoccupied molecular orbital to be essentially located on the iron atoms, largely of $3d$ character and being in-plane π antibonding in character [19]. So a distortion caused by an extra electron pair would be expected to break an Fe—Fe rather than an iron-to-bridging atom bond.

However the heavy atom core in II is highly distorted from an ideal square pyramid. The iron—iron non-bonding distance across the pyramidal face has an average of 3.54(1) Å and the phosphorus—phosphorus distance forming the other diagonal is ca. 1 Å shorter (2.587(5) Å average). This distortion is more pronounced than in $Fe_3(CO)_9S_2$ (VI) in which the Fe···Fe and S···S separations are 3.371(10) and 2.863(15) Å respectively. In II the mean Fe—Fe bonding distance is significantly larger than in VI (2.717(3) and 2.60(2) Å respectively) but the mean iron—heteroatom distance is shorter (Fe—P 2.218(5) Å in II and Fe—S 2.23(1) Å in VI). This iron—phosphorus distance is intermediate in distance between those reported for a single μ_3-PPh group in $H_2Fe_3(CO)_9(PPh)$

TABLE 1

FRACTIONAL ATOMIC COORDINATES (× 10^4) AND ISOTROPIC THERMAL PARAMETERS (× 10^3) FOR $Fe_3(CO)_9(PPh)_2$ with esd's in parentheses

Atom [a]	x/a	y/b	z/c	U
Fe(1A)	4253(2)	2161(2)	172(1)	
Fe(2A)	3455(2)	1905(2)	1848(1)	
Fe(3A)	3105(2)	3844(2)	1639(1)	
P(1A)	4705(3)	2898(3)	1269(3)	
P(2A)	2599(3)	2840(3)	779(3)	
C(1A)	5694(17)	1524(13)	18(12)	70(6)
O(1A)	6653(13)	1168(10)	−89(9)	100(5)
C(2A)	3583(14)	1402(12)	−424(11)	54(5)
O(2A)	3092(11)	955(9)	−836(9)	86(4)
C(3A)	4323(14)	3096(12)	−605(11)	55(5)
O(3A)	4339(11)	3759(9)	−1140(8)	82(4)
C(4A)	4110(14)	1870(11)	2842(11)	52(5)
O(4A)	4558(11)	1867(8)	3492(9)	79(4)
C(5A)	3923(17)	744(15)	1639(13)	76(6)
O(5A)	4330(13)	−35(11)	1548(10)	111(5)
C(6A)	2057(18)	1694(14)	2253(13)	80(6)
O(6A)	1097(15)	1569(11)	2497(10)	118(5)
C(7A)	1617(17)	4232(13)	1987(12)	68(6)
O(7A)	673(12)	4525(9)	2176(8)	82(4)
C(8A)	3671(17)	4107(14)	2587(14)	80(6)
O(8A)	4095(12)	4245(9)	3233(9)	92(4)
C(9A)	3387(14)	4848(12)	945(11)	56(5)
O(9A)	3597(10)	5459(9)	444(8)	78(4)
C(11A)	6161(7)	2936(7)	1645(6)	39(4)
C(12A)	6907(7)	2097(7)	1855(6)	51(4)
C(13A)	8011(7)	2139(7)	2171(6)	66(5)
C(14A)	8369(7)	3021(7)	2277(6)	72(6)
C(15A)	7624(7)	3861(7)	2067(6)	82(6)
C(16A)	6520(7)	3818(7)	1751(6)	59(5)
C(21A)	1133(7)	2770(8)	434(7)	48(4)
C(22A)	400(7)	3617(8)	225(7)	56(5)
C(23A)	−732(7)	3586(8)	−46(7)	74(6)
C(24A)	−1131(7)	2709(8)	−109(7)	62(5)
C(25A)	−398(7)	1862(8)	100(7)	63(5)
C(26A)	734(7)	1893(8)	371(7)	50(4)
Fe(1B)	446(2)	3474(2)	5809(1)	
Fe(2B)	504(2)	2214(2)	7246(1)	
Fe(3B)	1519(2)	1019(2)	6085(1)	
P(1B)	−112(3)	2035(3)	5953(3)	
P(2B)	1950(3)	2453(3)	6252(3)	
C(1B)	−1027(16)	4073(12)	5843(11)	58(5)
O(1B)	−1990(11)	4393(9)	5828(8)	78(4)
C(2B)	1044(15)	4474(13)	6131(11)	64(5)
O(2B)	1476(11)	5106(9)	6324(8)	82(4)
C(3B)	853(14)	3546(12)	4728(12)	57(5)
O(3B)	1134(11)	3556(9)	4003(9)	82(4)
C(4B)	−925(21)	2617(15)	7599(14)	94(7)
O(4B)	−1898(15)	2900(11)	7810(11)	122(6)
C(5B)	598(18)	1124(16)	7876(14)	87(7)
O(5B)	694(13)	409(11)	8304(10)	107(5)
C(6B)	1227(15)	2880(13)	7912(12)	64(5)
O(6B)	1699(12)	3310(9)	8327(9)	88(4)
C(7B)	2780(16)	387(13)	6543(12)	65(5)
O(7B)	3680(13)	8(10)	6812(9)	96(4)
C(8B)	766(15)	−10(12)	6111(11)	60(5)
O(8B)	250(11)	−665(9)	6083(8)	77(4)
C(9B)	1984(14)	1106(12)	5009(12)	56(5)

TABLE 1 (continued)

Atom[a]	x/a	y/b	z/c	U
O(9B)	2261(11)	1213(9)	4288(9)	84(4)
C(11B)	−1546(7)	1784(7)	5689(7)	44(4)
C(12B)	−2026(7)	2219(7)	4923(7)	60(5)
C(13B)	−3117(7)	2011(7)	4692(7)	72(6)
C(14B)	−3727(7)	1369(7)	5227(7)	74(6)
C(15B)	−3247(7)	934(7)	5993(7)	64(5)
C(16B)	−2156(7)	1142(7)	6224(7)	59(5)
C(21B)	3393(7)	2754(8)	6409(7)	44(4)
C(22B)	4051(7)	2313(8)	7097(7)	60(5)
C(23B)	5162(7)	2572(8)	7211(7)	76(6)
C(24B)	5616(7)	3272(8)	6637(7)	74(6)
C(25B)	4958(7)	3713(8)	5949(7)	82(6)
C(26B)	3847(7)	3454(8)	5835(7)	60(5)

[a] The A and B in the atom numbering scheme identify the two molecules in the asymmetric unit. In molecule A the carbon atoms of the phenyl group are labelled C(IJA) where I(1,2) indicates the ring and J(1,6) the atoms of the ring.
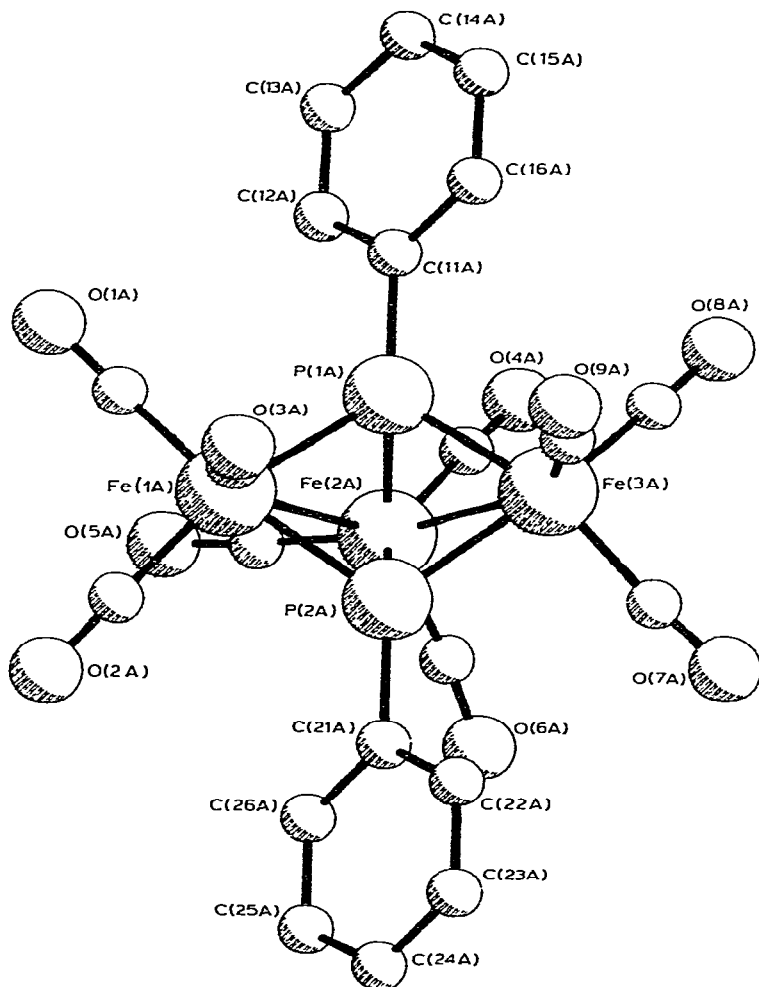

Fig. 1. $Fe_3(CO)_9(PPh)_2$ (molecule A) excluding H atoms.

TABLE 2

ANISOTROPIC THERMAL PARAMETERS ($\times 10^4$) FOR $Fe_3(CO)_9(PPh)_2$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1A)	435(15)	423(15)	388(14)	—56(12)	—7(11)	—75(11)
Fe(2A)	365(14)	472(15)	373(14)	32(12)	—24(11)	—88(11)
Fe(3A)	377(14)	474(15)	461(15)	—95(12)	—30(11)	2(11)
P(1A)	355(25)	405(26)	380(25)	—4(21)	—64(20)	—71(20)
P(2A)	362(25)	512(29)	395(26)	—27(22)	—32(20)	—71(21)
Fe(1B)	467(15)	353(14)	427(15)	—55(11)	—27(11)	—26(12)
Fe(2B)	397(15)	527(16)	348(14)	—44(12)	—11(11)	—85(12)
Fe(3B)	420(14)	386(14)	427(14)	—28(12)	—13(11)	—42(11)
P(1B)	392(26)	359(26)	387(25)	—66(21)	—13(20)	—34(20)
P(2B)	411(26)	369(26)	382(26)	—75(21)	—3(20)	—72(20)

Anisotropic temperature factor of the form $\exp(-8\pi^2(h^2a^{*2}U_{(1,1)} + ... + 2hka^*b^*U_{(1,2)} + ...))$.

TABLE 3

SELECTED BOND LENGTHS (Å) AND BOND ANGLES (deg) FOR $Fe_3(CO)_9(PPh)_2$

| Bond lengths	Molecule A	Molecule B
Fe(1)—Fe(2)	2.718(3)	2.714(3)
Fe(2)—Fe(3)	2.717(3)	2.717(3)
Fe(1)—P(1)	2.216(5)	2.202(4)
Fe(1)—P(2)	2.216(5)	2.199(5)
Fe(2)—P(1)	2.222(4)	2.225(5)
Fe(2)—P(2)	2.214(4)	2.231(5)
Fe(3)—P(1)	2.211(5)	2.214(5)
Fe(3)—P(2)	2.207(5)	2.199(4)
P(1)—C(11)	1.810(8)	1.804(8)
P(2)—C(21)	1.811(8)	1.796(8)
Fe—C (max)	1.79(2)	1.79(2)
(min)	1.71(2)	1.72(2)
C—O (max)	1.19(2)	1.18(2)
(min)	1.14(2)	1.14(2)
C—C (constrained during refinement)	1.395	1.395
Bond angles		
Fe(1)—Fe(2)—Fe(3)	81.7(1)	81.2(1)
Fe(1)—P(1)—Fe(3)	106.8(2)	106.3(2)
Fe(1)—P(2)—Fe(3)	107.0(2)	106.9(2)
P(1)—Fe(1)—P(2)	71.4(2)	72.0(2)
P(1)—Fe(2)—P(2)	71.3(2)	71.0(2)
P(1)—Fe(3)—P(2)	71.7(2)	71.8(2)
Fe(1)—P(1)—C(11)	127.1(4)	123.9(4)
Fe(1)—P(2)—C(21)	124.8(4)	125.1(4)
Fe(2)—P(1)—C(11)	124.6(4)	128.0(4)
Fe(2)—P(2)—C(21)	124.7(4)	128.0(4)
Fe(3)—P(1)—C(11)	124.9(4)	127.5(4)
Fe(3)—P(2)—C(21)	126.9(4)	125.7(4)
Fe—C—O (max)	178.2(1.5)	179.1(1.7)
(min)	173.2(1.8)	174.9(1.6)
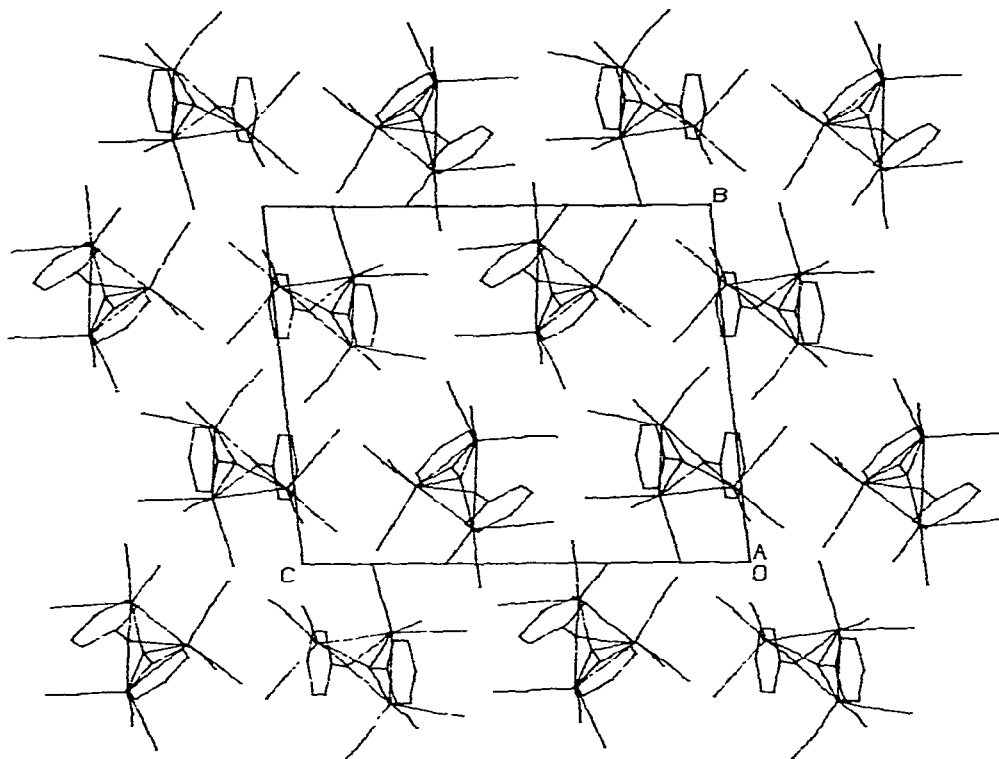
Fig. 2. Molecular packing arrangement viewed down the a direction with the molecules shown as line drawings.

(I), average 2.17(2) Å [1], and in a di μ_4-P-*para*-tolyl bridged species $Fe_4(CO)_{11}$-(P-p-tolyl)$_2$ (VIII) [3] (average 2.28(4) Å). Complex VIII also exhibits a reasonably short phosphorus—phosphorus distance (2.636(4) Å), although this is ca 0.05 Å larger than in II. While this suggests a marked P—P interaction, these distances are still over 0.3 Å larger than the P—P bond lengths in (PhP)$_5$ [20] and (PhP)$_6$ [21].

This work further demonstrates the versatility of bridging P—R ligands in stabilising chained and triangular trinuclear clusters and arrays of metal atoms with tetragonal faces.

Acknowledgements

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