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THE CRYSTAL AND MOLECULAR STRUCTURE OF TRICYCLIC TETRACARBONYLIRON CARBONYLTRIS(TRIPHENYLPHOSPHITE)-DIPLATINUM

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Summary

A single crystal X-ray structure analysis of $FePt_2(CO)_5[P(OPh)_3]_3$ has been carried out in order to clarify its stereochemistry. The complex crystallizes in the triclinic space group $P\bar{1}$ with $a = 22.80(2)$, $b = 12.31(1)$, $c = 10.55(1)$ Å, $\alpha = 105.2(1)°$, $\beta = 78.0(1)°$, $\gamma = 88.6(1)°$, $Z = 2$. Diffractometer data have been refined by least-squares methods to a final R of 0.062 for 2353 reflections. The molecule contains a triangular $FePt_2$ cluster to which the ligands are bound as follows: four CO groups about iron in distorted octahedral geometry, the fifth carbonyl and the phosphite ligands about the platinums giving distorted square-planar geometries. The metal—metal distances in the cluster are shorter than expected for single bonds with values of 2.633(1) Å for Pt—Pt, and 2.550(5), 2.583(6) Å for Fe—Pt. The platinum—phosphite interactions have a mean value of 2.22 Å, and are shorter than the platinum—phosphine distances found in a variety of structures.

Introduction

The syntheses of carbonyl mixed metal atom clusters containing platinum and iron, with a variety of tertiary phosphines, phosphites and arsines as ligands, have been recently described [1]. The complexes have the compositions $Fe_2Pt(CO)_{10-n}L_n$ ($n = 1,2$) and $FePt_2(CO)_5[P(OPh)_3]_3$; similar compounds with ruthenium and osmium replacing iron have also been prepared [2].

The structures of these complexes have been suggested on the basis of their IR and NMR spectra and, for $Fe_2Pt(CO)_9(PPh_3)$, confirmed by an X-ray crystallographic study [3]. This complex consists of two $Fe(CO)_4$ and one $Pt(CO)(PPh_3)$ moieties linked in a triangular cluster, the coordinations around the iron atoms and the platinum atom being octahedral and square-planar, respectively.

We report here the single crystal X-ray structure of $FePt_2(CO)_5[P(OPh)_3]_3$, which has allowed clarification of the complete stereochemistry of the compound, especially the positions of the phosphite ligands and the bonding geometry of the carbonyl groups; the latter were expected to be linear in this complex and partially bridged in the ruthenium and osmium analogues. A preliminary communication concerning this work has already appeared [4].

Experimental

Crystal data

$C_{59}H_{45}FeO_{14}P_3Pt_2$, $M = 1515.9$, triclinic, $a = 22.80(2)$, $b = 12.31(1)$, $c = 10.55(1)$ Å, $\alpha = 105.2(1)°$, $\beta = 78.0(1)°$, $\gamma = 88.6(1)°$, $U = 2785.7$ Å^3, $D_m = 1.77(2)$ (by flotation), $Z = 2$, $D_c = 1.81$, $F(000) = 1476$. Space group $P\bar{1}$. Silicon monochromatized Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 56.9 cm^{-1}. Unit cell dimensions were obtained from precession photographs and refined on a Pailred diffractometer. The orange crystals were stable to X-irradiation.

Measurement of intensities

A prismatic crystal, with dimensions 0.33 × 0.28 × 0.18 mm, was mounted on a Pailred linear equi-inclination diffractometer. Intensities were monitored by ω-scan technique at a rate of 0.5°/min with stationary crystal-stationary counter background counts of 40 s taken on each side of the scan. Increasing scan ranges, from 0.8° to 2.0°, were used for ω with increasing μ. The integrated intensities were corrected for Lorentz and polarization factors, the latter being evaluated taking account of the partial polarization of the incident beam [5]. The calculated transmission coefficients, obtained with the Busing and Levy method [6], were found in the range 0.37 - 0.57, and the absorption corrections were performed using an 8^3 sampling of the crystal. No extinction corrections were made.

Measurements were made in the reciprocal lattice levels hk0-8, for all reflections with $2° \leqslant \theta \leqslant 25°$ and resulted in 2353 intensities with $\sigma(I)/I \leqslant 0.25$. No systematic variations of the intensities of four well-spaced zero-level reflections, measured after completion of each layer, were observed.

Determination and refinement of the structure

A tridimensional Patterson function showed the peaks expected for a triangular arrangement of the $FePt_2$ group. A Fourier synthesis phased by these atoms allowed the determination of the phosphorus positions. After preliminary least squares refinement of the $FePt_2P_3$ moiety, a difference synthesis showed the peaks of carbon and oxygen atoms. The whole structure was refined by block-diagonal least-squares with the C_6H_5 groups constrained to the ideal geometry: C—C 1.392, C—H 1.08 Å, C—C—C and C—C—H 120°. The thermal motion was treated anisotropically for the atoms of the $FePt_2P_3$ moiety and isotropically for carbons and oxygens. The hydrogen atoms were assigned the same thermal factors as the corresponding carbons.

After convergence of this model to $R = 0.062$ and $R' = 0.076$ {$R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$}, relaxation of the rigid body contraints was attempted in the hope of detecting the probable deformations of the phenyl rings caused by the oxygen—phenyl interactions. Unfortunately, distances and angles in the rings proved to be too scattered and no systematic effects were detectable, probably because of the insufficiency and quality of the data. The unconstrained model was therefore rejected.

The observations were weighted according to the formula $w = 1/(A + B\cdot F_o + C\cdot F_o^2)$, where in the final cycles A, B and C had values 15.0, 0.4 and 0.0006, and were chosen on the basis of analysis of $\Sigma w\cdot\Delta^2$. The atomic scattering factors were taken from ref. 7 for platinum, iron (corrected for the real and immaginary part of the anomalous dispersion), phosphorus, oxygen and carbon, and from ref. 8 for hydrogen. The function $\Sigma w(F_o - k|F_c|)^2$ was minimized.

A final difference Fourier synthesis did not reveal unusual features; the highest peaks were of about 2 $e/\text{Å}^3$, located in the vicinity of the platinum atoms. The results of the refinement are reported in Tables 1 and 2. The final list of the observed and computed structure factors moduli can be obtained on application to the authors.

Computations

All computations were performed on a UNIVAC 1106 computer. The transmission factors were calculated by use of a local programme, in which the directions of primary and diffracted beams are evaluated as described in ref. 9. Counter data reduction and statistical analysis for weighting schemes were also based upon Fortran programmes written in our laboratory. In addition, local versions of entries Nos. 7528, 7531, 7532 and 7535 in the 1966 "International World List of Crystallographic Programs" were used for Fourier analysis, structure factors, and least squares calculations.

Crystal and molecular structure and discussion

The crystal structure, shown in Fig. 1, consists of discrete molecules of $FePt_2(CO)_5[P(OPh)_3]_3$; the intermolecular distances indicate normal Van der Waals contacts falling in the same range as the intramolecular ones listed in Table 3.

The molecule contains a triangular $FePt_2$ cluster to which the ligands are bound as follows: four CO groups lie about the iron atom in such a way that the resulting coordination is distorted octahedral; the fifth carbonyl group is bound to Pt(1) *trans* to iron, and the three phosphite ligands occupy coordination sites about the platinum atoms giving distorted square planar geometries. The deviations of C(1), P(1), P(2), and P(3) from the $FePt_2$ plane are moderate, − 0.32, +0.17, − 0.04, and +0.06 Å respectively, and are attributable to packing effects.

An obvious cause of distorsion in the coordination about the metals is the triangular geometry of the cluster that imposes intermetallic angles of about 60°. Of major interest, however, is the angular deformation of both the apical CO's bound to iron which markedly incline towards the platinums [C(3)—Fe—C(5) angle 144°], reaching short Pt···C contacts in the range 2.57 - 2.82 Å. An inspection of the non-bonded contacts shows not only that this deformation is not caused by intermolecular interactions, but also that intramolecular carbonyl—phenyl contacts (reported in Table 3) prevent a more pro-

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TABLE 1

POSITIONAL AND THERMAL PARAMETERS FOR THE $FePt_2P_3$ MOIETY[a,b]

Atom	x	y	z	β_{11}[c]	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Pt(1)	1770 (0)	−1528 (1)	−3176 (1)	10 (0)	−2 (0)	−18 (1)	67 (1)	41 (2)	106 (1)
Pt(2)	2651 (0)	−2845 (1)	−4985 (1)	8 (0)	0 (0)	−15 (1)	68 (1)	62 (1)	105 (1)
Fe	1940 (1)	−1526 (4)	−5642 (4)	13(1)	−4 (3)	−32 (3)	94 (4)	89 (7)	113 (5)
P(1)	1027 (3)	− 156 (7)	−2209 (9)	13 (1)	−7 (6)	−20 (7)	76 (7)	21 (14)	99 (10)
P(2)	3278 (3)	−3748 (7)	−6903 (9)	4 (1)	6 (6)	−13 (6)	87 (8)	29 (15)	116 (11)
P(3)	3007 (3)	−3572 (8)	−3573 (9)	13 (1)	−4 (6)	−21 (6)	96 (8)	54 (14)	92 (10)

[a] All values X 10^4. [b] The numbers in parentheses here and in the succeeding tables are the estimated standard deviations on last significant digits. [c] The β_{ij} values are the coefficients of: $\exp[-(h^2\cdot\beta_{11} + k^2\cdot\beta_{22} + l^2\cdot\beta_{33} + h\cdot k\cdot\beta_{12} + h\cdot l\cdot\beta_{13} + k\cdot l\cdot\beta_{23})]$.

TABLE 2

POSITIONAL AND THERMAL PARAMETERS OF THE LIGHT ATOMS[a]

Atom	x	y	z	B(Å^2)
C(1)	1771 (14)	−2075 (26)	−1610 (33)	3.9 (7)
O(1)	1696 (12)	−2325 (22)	−642 (28)	6.9 (7)
C(2)	1311 (14)	−690 (26)	−5644 (33)	4.1 (7)
O(2)	935 (11)	−21 (21)	−5694 (26)	6.3 (6)
C(3)	1572 (16)	−2803 (29)	−5666 (37)	4.9 (8)
O(3)	1281 (10)	−3565 (18)	−5674 (23)	5.2 (5)
C(4)	2282 (17)	−1700 (32)	−7418 (41)	6.1 (9)
O(4)	2430 (11)	−1886 (20)	−8506 (26)	6.2 (6)
C(5)	2412 (17)	− 616 (31)	−4859 (40)	5.7 (9)
O(5)	2678 (11)	141 (20)	−4439 (26)	6.1 (6)
O(6)	984 (10)	507 (19)	−725 (24)	5.1 (5)
O(7)	982 (9)	837 (17)	−2895 (22)	4.5 (5)
O(8)	329 (11)	− 538 (20)	−2031 (25)	5.7 (6)
O(9)	3885 (9)	−3170 (17)	−7416 (22)	4.4 (5)
O(10)	3571 (8)	−4946 (15)	−6903 (19)	3.3 (4)
O(11)	3086 (10)	−4079 (18)	−8321 (23)	5.2 (5)
O(12)	3652 (9)	−4287 (17)	−4173 (22)	4.4 (5)
O(13)	3125 (8)	−2753 (15)	−2228 (19)	3.3 (4)
O(14)	2591 (8)	−4354 (16)	−2827 (20)	3.7 (4)
C(6)	1447 (10)	762 (27)	−113 (25)	5.1 (8)
C(7)	1936 (10)	1230 (23)	−744 (21)	7.0 (11)
C(8)	2418 (10)	1502 (24)	−132 (28)	8.2 (12)
C(9)	2412 (10)	1304 (27)	1111 (25)	6.4 (10)
C(10)	1925 (10)	835 (23)	1740 (21)	7.1 (11)
C(11)	1442 (10)	564 (24)	1130 (28)	6.7 (10)
C(12)	572 (10)	1753 (17)	−2442 (27)	4.2 (7)
C(13)	−25 (11)	1667 (15)	−2527 (28)	5.9 (9)
C(14)	−421 (8)	2636 (22)	−2136 (29)	6.6 (10)
C(15)	−216 (10)	3689 (17)	−1665 (27)	5.6 (9)
C(16)	381 (11)	3775 (15)	−1580 (28)	6.1 (9)
C(17)	776 (8)	2807 (22)	−1966 (29)	5.5 (9)
C(18)	193 (13)	−1584 (16)	−2430 (22)	3.1 (6)
C(19)	163 (9)	−2308 (21)	−1607 (18)	5.6 (9)
C(20)	−15 (11)	−3391 (18)	−2034 (23)	7.4 (11)
C(21)	−164 (13)	−3750 (16)	−3282 (22)	6.9 (10)
C(22)	−133 (9)	−3028 (21)	−4108 (18)	6.8 (10)
C(23)	44 (11)	−1944 (18)	−3680 (23)	5.1 (8)
C(24)	3904 (14)	−2070 (14)	−7230 (20)	3.4 (6)
C(25)	4044 (13)	−1297 (16)	−6133 (21)	6.2 (10)
C(26)	4057 (13)	−161 (16)	−6100 (21)	7.7 (11)
C(27)	3929 (14)	204 (14)	−7162 (20)	7.2 (11)
C(28)	3789 (13)	− 567 (16)	−8259 (21)	6.4 (10)
C(29)	3776 (13)	−1704 (16)	−8292 (21)	6.3 (10)
C(30)	3932 (9)	−5716 (17)	−7950 (22)	4.2 (7)
C(31)	4525 (10)	−5531 (14)	−8450 (23)	4.3 (7)
C(32)	4902 (7)	−6391 (20)	−9424 (23)	3.9 (7)
C(33)	4688 (9)	−7434 (17)	−9896 (22)	5.3 (8)
C(34)	4096 (10)	−7620 (14)	−9397 (23)	5.8 (9)
C(35)	3717 (7)	−6760 (20)	−8423 (23)	5.4 (9)
C(36)	2565 (10)	−4657 (24)	−8520 (22)	5.7 (9)
C(37)	2280 (8)	−5323 (22)	−7735 (20)	5.3 (9)
C(38)	1784 (10)	−5876 (20)	−8058 (23)	4.4 (7)
C(39)	1571 (10)	−5760 (24)	−9164 (22)	5.8 (9)
C(40)	1855 (8)	−5093 (22)	−9949 (20)	7.0 (10)
C(41)	2352 (10)	−4541 (20)	−9625 (23)	6.1 (9)
C(42)	3913 (13)	−5020 (19)	−3637 (23)	3.3 (6)
C(43)	4332 (12)	−5789 (14)	−4639 (17)	5.8 (9)
C(44)	4622 (10)	−6664 (16)	−4331 (22)	8.1 (12)
C(45)	4492 (13)	−6769 (19)	−3023 (23)	6.7 (10)
C(46)	4073 (12)	−6000 (14)	−2020 (17)	6.6 (10)
C(47)	3783 (10)	−5126 (16)	−2328 (22)	4.8 (8)
C(48)	3519 (11)	−1941 (20)	−2294 (28)	4.6 (8)
C(49)	3336 (9)	− 892 (24)	−2414 (31)	5.5 (9)
C(50)	3738 (12)	−57 (17)	−2403 (31)	8.0 (12)

(continued)

TABLE 2(continued)

POSITIONAL AND THERMAL PARAMETERS OF THE LIGHT ATOMS[a]

Atom	x	y	z	
C(51)	4321 (11)	—270 (20)	—2273 (28)	6.7 (10)
C(52)	4504 (9)	—1318 (24)	—2153 (31)	8.0 (12)
C(53)	4103 (12)	—2154 (17)	—2164 (31)	6.2 (9)
C(54)	2318 (11)	—5206 (20)	—3562 (26)	4.0 (7)
C(55)	1751 (11)	—4940 (15)	—3752 (27)	6.5 (10)
C(56)	1449 (9)	—5777 (23)	—4461 (28)	6.5 (10)
C(57)	1714 (11)	—6879 (20)	—4977 (26)	6.8 (10)
C(58)	2281 (11)	—7145 (15)	—4787 (27)	7.4 (11)
C(59)	2583 (9)	—6308 (23)	—4079 (28)	6.7 (10)
H(7)[b]	1942	1384	—1712	
H(8)	2798	1868	—623	
H(9)	2788	1515	1589	
H(10)	1921	681	2707	
H(11)	1062	201	1624	
H(13)	—183	847	—2898	
H(14)	—887	2572	—2199	
H(15)	— 523	4443	—1364	
H(16)	541	4596	—1211	
H(17)	1243	2875	—1897	
H(19)	279	—2029	—634	
H(20)	—39	—3955	—1393	
H(21)	—304	—4593	—3611	
H(22)	—247	—3308	—5083	
H(23)	68	—1379	—4320	
H(25)	4144	—1579	—5304	
H(26)	4168	440	—5246	
H(27)	3938	1090	—7134	
H(28)	3690	—284	—9087	
H(29)	3666	—2303	—9146	
H(31)	4693	—4718	—8081	
H(32)	5364	—6247	—9814	
H(33)	4984	—8102	—10653	
H(34)	3930	—8434	—9767	
H(35)	3256	—6903	—8032	
H(37)	2445	—5412	—6870	
H(38)	1564	—6396	—7448	
H(39)	1184	—6190	—9414	
H(40)	1690	—5004	—10811	
H(41)	2574	—4020	—10234	
H(43)	4434	—5706	—5657	
H(44)	4949	—7262	—5111	
H(45)	4719	—7450	—2784	
H(46)	3973	—6082	—1000	
H(47)	3457	—4527	—1548	
H(49)	2882	—726	—2515	
H(50)	3597	759	—2496	
H(51)	4634	379	—2264	
H(52)	4959	—1482	—2050	
H(53)	4247	—2970	—2072	
H(55)	1546	—4082	—3348	
H(56)	1009	—5569	—4610	
H(57)	1480	—7531	—5527	
H(58)	2487	—8002	—5191	
H(59)	3024	—6515	—3929	

[a] $x, y, z \times 10^4$. [b] The hydrogen atoms have the same labels and the same thermal parameters of the corresponding phenyl carbon atoms.

nounced bending of these ligands. It can be concluded that the carbonyl groups tend to establish bonding interactions with the platinum orbitals directed above and below the plane of the cluster; very probably in the presence of less bulky ligands these interactions could become much more effective.

The Fe—Pt distances are slightly but significantly different, that *trans* to

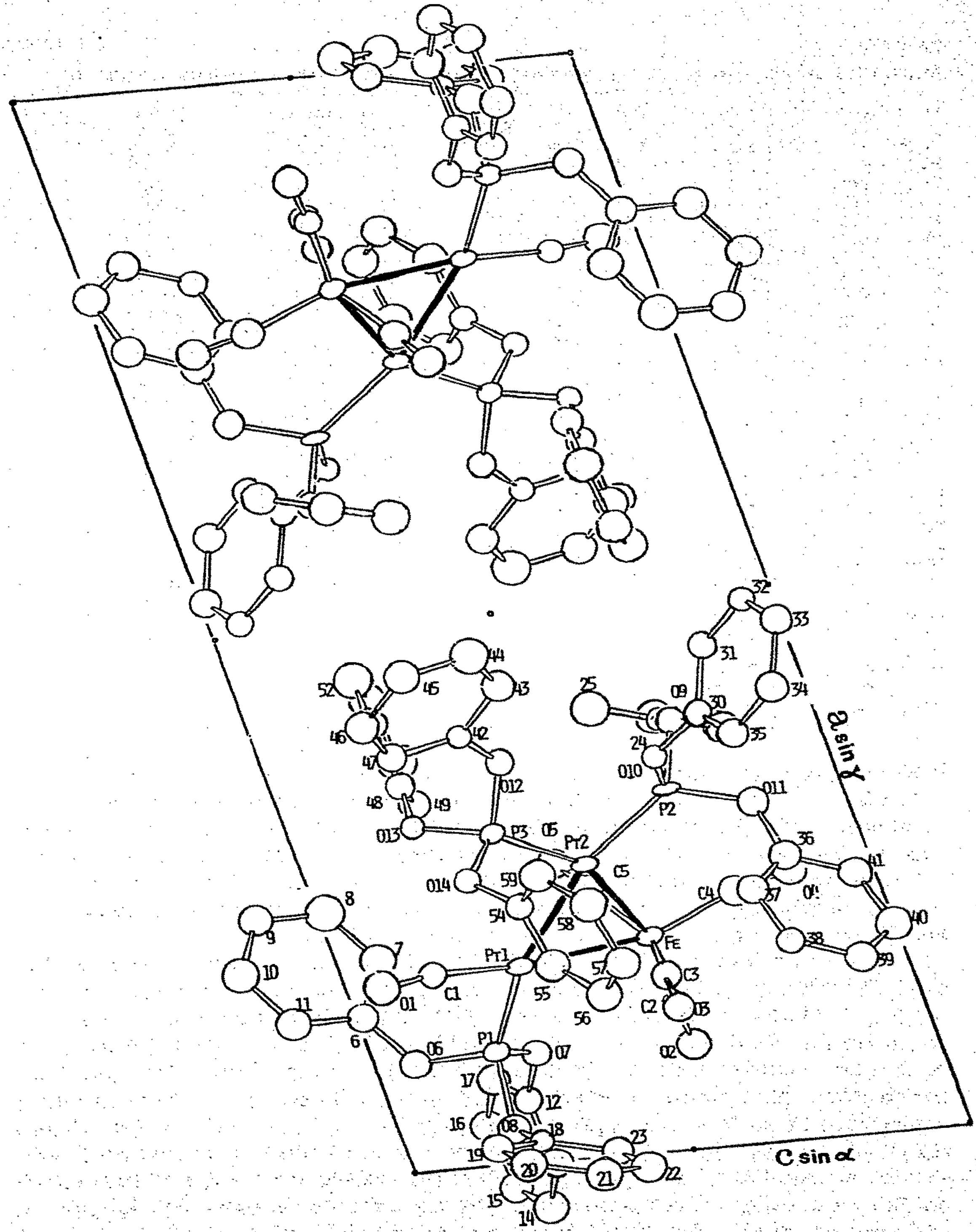

Fig. 1. Projection of the content of the unit cell down the *b* axis. For sake of clarity the hydrogen atoms are not reported and the phenyl carbons are indicated by their numbers only.

TABLE 3

BOND DISTANCES AND SELECTED INTRAMOLECULAR CONTACTS (Å) IN THE MOLECULE

Pt(1) —Pt(2)	2.633 (1)	C(1) ···O(13)	3.07 (4)
Pt(1) —Fe	2.550 (5)	C(1) ···O(14)	3.14 (4)
Pt(2) —Fe	2.583 (6)	C(1) ···H(55)	2.80 (5)
Pt(1) —P(1)	2.236 (8)	O(2) ···O(7)	2.89 (4)
Pt(2) —P(2)	2.217 (8)	C(3) ···Pt(1)	2.82 (4)
Pt(2) —P(3)	2.202 (9)	C(3) ···Pt(2)	2.70 (4)
Pt(1) —C(1)	1.94 (4)	C(5) ···Pt(1)	2.57 (4)
Fe —C(2)	1.75 (3)	C(5) ···Pt(2)	2.75 (4)
Fe —C(3)	1.80 (4)	C(3) ···C(37)	3.43 (4)
Fe —C(4)	1.83 (4)	O(3) ···C(37)	3.14 (4)
Fe —C(5)	1.74 (4)	O(3) ···H(55)	2.86 (5)
C(1) —O(1)	1.12 (5)	O(4) ···C(29)	3.13 (4)
C(2) —O(2)	1.19 (4)	O(4) ···C(41)	3.19 (4)
C(3) —O(3)	1.16 (4)	O(4) ···H(29)	2.76 (5)
C(4) —O(4)	1.09 (5)	O(4) ···H(41)	2.75 (5)
C(5) —O(5)	1.17 (5)	C(5) ···H(49)	2.92 (5)
P(1) —O(6)	1.55 (2)	O(5) ···H(49)	2.64 (5)
P(1) —O(7)	1.59 (3)	O(8) ···H(13)	2.51 (5)
P(1) —O(8)	1.66 (3)	O(8) ···H(23)	2.57 (5)
P(2) —O(9)	1.63 (2)	O(9) ···C(30)	3.03 (4)
P(2) —O(10)	1.60 (2)	O(9) ···C(31)	3.04 (4)
P(2) —O(11)	1.60 (3)	O(9) ···H(31)	2.47 (5)
P(3) —O(12)	1.61 (2)	O(10)···H(37)	2.64 (5)
P(3) —O(13)	1.59 (2)	O(11)···C(30)	2.91 (5)
P(3) —O(14)	1.61 (2)	O(12)···C(48)	3.01 (5)
O(6) —C(6)	1.35 (4)	O(13)···H(47)	2.61 (6)
O(7) —C(12)	1.36 (3)	O(14)···C(42)	2.99 (5)
O(8) —C(18)	1.31 (3)	O(14)···H(47)	2.64 (5)
O(9) —C(24)	1.32 (3)		
O(10)—C(30)	1.35 (2)		
O(11)—C(36)	1.42 (4)		
O(12)—C(42)	1.37 (4)		
O(13)—C(48)	1.37 (3)		
O(14)—C(54)	1.38 (3)		

P(3) being 0.033 Å longer than the other *trans* to the carbonyl group. Comparable distances, 2.526 and 2.605 Å, and the same type of asymmetry, but more pronounced (0.079 Å), are present in $Fe_2Pt(CO)_9(PPh_3)$. A rationalization of this difference could be that the σ—π bonding ability of the carbonyl group is comparable with that of the triphenylphosphite to a greater extent than that of the triphenylphosphine; consequently, the bonding situations *trans* to CO and $P(OPh)_3$ are also more similar.

The bond distances in the cluster are shorter than would be expected for single bonds estimated from the atomic radii of iron and platinum in the metals, 1.24 and 1.39 Å respectively [10]. If the radius of iron is estimated from the Fe—Fe distance in $Fe_2Pt(CO)_9(PPh_3)$, 2.78 Å, the bond shortening is even more marked. Our Pt—Pt value, 2.633(1) Å, is significantly shorter than the average value found in $Pt_4(CO)_5(PPhMe_2)_4$, 2.76 Å [11], but compares better with those found in $Pt_2S(CO)(PPh_3)_3$, 2.65 Å [12], and in $Pt_3(SnCl_3)_2(C_8H_{12})_3$, 2.58 Å [13]. The molecular structure of the latter compound consists of an equilateral triangle of platinum atoms, each coordinated to the two double bonds of a cyclooctadiene molecule and to the two $SnCl_3$ groups, which are bridging above and below the triangle. $Pt_3(SnCl_3)_2(C_8H_{12})_3$ and our complex have the same number of valency electrons (44) and the qualitative model of molecular orbitals proposed for the Pt_3 cluster [11] can be applied for the rationalization of the bonds in the $FePt_2$ cluster. The model

TABLE 4

RELEVANT BOND ANGLES (°) IN THE MOLECULE

Pt(1)—Fe —Pt(2)	61.7 (1)	O(7) —P(1) —O(6)	102 (1)
Pt(1)—Pt(2)—Fe	58.5 (1)	O(7) —P(1) —O(8)	101 (1)
Pt(2)—Pt(1)—Fe	59.8 (1)	O(6) —P(1) —O(8)	98 (1)
Pt(2)—Pt(1)—P(1)	160.9 (3)	O(9) —P(2) —O(10)	100 (1)
Pt(1)—Pt(2)—P(2)	163.5 (3)	O(9) —P(2) —O(11)	96 (1)
Pt(2)—Pt(1)—C(1)	101.7 (8)	O(10)—P(2) —O(11)	101 (1)
C(1) —Pt(1)—P(1)	97.4 (9)	O(12)—P(3) —O(13)	101 (1)
P(1) —Pt(1)—Fe	101.6 (3)	O(12)—P(3) —O(14)	105 (1)
Pt(1)—Pt(2)—P(3)	96.4 (2)	O(13)—P(3) —O(14)	95 (1)
P(3) —Pt(2)—P(2)	100.1 (3)	P(1) —O(6) —C(6)	127 (2)
P(2) —Pt(2)—Fe	105.0 (3)	P(1) —O(7) —C(12)	127 (2)
Pt(1)—Fe —C(2)	102 (1)	P(1) —O(8) —C(18)	124 (2)
Pt(2)—Fe —C(4)	102 (1)	P(2) —O(9) —C(24)	123 (2)
Pt(1)—Fe —C(3)	79 (1)	P(2) —O(10)—C(30)	127 (2)
Pt(2)—Fe —C(3)	74 (1)	P(2) —O(11)—C(36)	123 (2)
Pt(1)—Fe —C(5)	71 (1)	P(3) —O(12)—C(42)	127 (2)
Pt(2)—Fe —C(5)	76 (1)	P(3) —O(13)—C(48)	120 (2)
C(3) —Fe —C(5)	144 (2)	P(3) —O(14)—C(54)	120 (2)
C(2) —Fe —C(4)	94 (2)	O(6) —C(6) —C(9)	179 (2)
C(3) —Fe —C(2)	97 (2)	O(7) —C(12)—C(15)	176 (2)
C(3) —Fe —C(4)	103 (2)	O(8) —C(18)—C(21)	176 (2)
C(5) —Fe —C(2)	107 (2)	O(9) —C(24)—C(27)	173 (2)
C(5) —Fe —C(4)	101 (2)	O(10)—C(30)—C(33)	174 (2)
Pt(1)—C(1) —O(1)	171 (3)	O(11)—C(36)—C(39)	174 (2)
Fe —C(2) —O(2)	171 (3)	O(12)—C(42)—C(45)	170 (2)
Fe —C(3) —O(3)	173 (3)	O(13)—C(48)—C(51)	177 (2)
Fe —C(4) —O(4)	171 (4)	O(14)—C(54)—C(57)	177 (2)
Fe —C(5) —O(5)	167 (4)		
Pt(1)—P(1) —O(6)	118 (1)		
Pt(1)—P(1) —O(7)	118 (1)		
Pt(1)—P(1) —O(8)	117 (1)		
Pt(2)—P(2) —O(9)	119 (1)		
Pt(2)—P(2) —O(10)	114 (1)		
Pt(2)—P(2) —O(11)	123 (1)		
Pt(2)—P(3) —O(12)	116 (1)		
Pt(2)—P(3) —O(13)	119 (1)		
Pt(2)—P(3) —O(14)	118 (1)		

shows that the metal—metal bond order is intermediate between one and two and also that the deficiency of four electrons in the compound, based on the assumption of M—M electron pair bonds, is formal since the lowest unfilled molecular orbital is antibonding in character.

The Pt—C(1) distance, 1.94(4) Å, can be compared with those found in $Fe_2Pt(CO)_9(PPh_3)$, 1.94(1) Å [3], in $Pt(CO)_2(PPh_2Et)_2$, 1.92(2) Å [14], in the monoclinic, 1.86(3) [15], and trigonal, 1.84(2) Å [16], polymorphs of $Pt(CO)(PPh_3)_3$, in $PtCl(PEt_3)_2(CO)]^+$, 1.78 Å [17] and in $PtCl_2(ONC_2H_4\text{-}OCH_3)(CO)$, 1.74(4) Å [18].

The C—O distance, 1.12(5) Å, is normal but its high estimated standard deviation does not allow useful comparisons with other experimental values. The equatorial and axial iron—carbonyl interactions do not reveal significant differences and the mean values, 1.78(2) and 1.15(3) Å for Fe—C and C—O distances, are in the range of the expected values.

Of particular interest are the platinum—phosphorus interactions. The differences among them are probably chemically significant, but their average, 2.22 Å, is more useful for discussion. We are not aware of other reports of platinum—phosphite distances; however a comparison with the Pt—P distance in $Fe_2Pt(CO)_9(PPh_3)$, 2.30 Å, and with the great variety of other experimental

TABLE 5

COMPARISON OF THE BONDING PARAMETERS (MEAN VALUES) FOR THE $P(OPh)_3$ LIGAND IN SOME COMPOUNDS

Compound	P—O(Å)	O—Ph(Å)	M—P—O(°)	O—P—O(°)	P—O—Ph(°)	Ref.
$FePt_2(CO)_5[P(OPh)_3]_3$	1.60	1.36	118	100	124	This work
$Cr(CO)_4[P(OPh)_3]_2$	1.60	1.40	117	101	126	19
$Cr(CO)_5[P(OPh)_3]$	1.60	1.40	118	100	127	21
$Rh_2Cl_2(C_8H_{12})[P(OPh)_3]_2$	1.60	1.41	118	100	125	22
$OP(OPh)_3$	1.63	—	115	104	122	23
$IrCl[P(OPh)_2(OC_6H_4)]_2[P(OPh)_3]$	1.59	1.41	114	104	128	20

values shows that the platinum—phosphite distances are shorter than the platinum—phosphine ones. On the basis of the σ—π bonding theory a phosphite ligand should be less basic but more acid than phosphines because of the electron withdrawal effect of the electronegative oxygens attached to phosphorus. This synergic mechanism and some degree of contraction of the phosphorus orbitals caused by the polarity of the P—O bonds, may explain the bond shortening. Similar explanations have been already put forward by Preston et al. [19], and by Guss and Mason [20].

The principal bonding parameters in the triphenylphosphite ligands are reported in Table 5 together with other experimental values. All the values are strictly comparable except the oxygen—phenyl distance which, in our structure, is 0.04 Å shorter. Very probably this difference originates from the refinement techniques used for the phenyl rings. In the other structures the atoms have been refined individually whilst, as described in the experimental section, we have used an ideal rigid model of C_6H_5 which now proves not to be fully adequate.

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