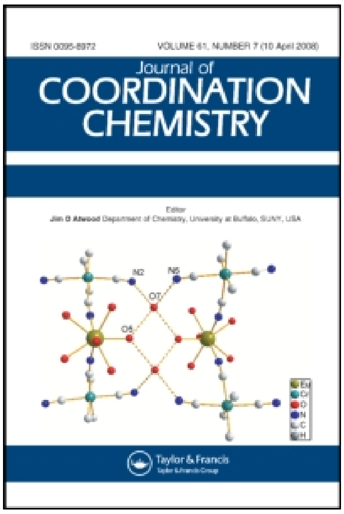

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SYNTHESIS OF A DINUCLEAR YLID COMPLEX DERIVED FROM $P(OPh)_3$: CRYSTAL STRUCTURES OF $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHP(OPh)_3)][BF_4^-]$ AND $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPPh_3)][BF_4^-]$

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SYNTHESIS OF A DINUCLEAR YLID COMPLEX DERIVED FROM P(OPh)$_3$: CRYSTAL STRUCTURES OF [Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CHP(OPh)$_3$)$^+$][BF$_4^-$] AND [Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CHPPh$_3$)$^+$][BF$_4^-$]

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[Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CHP(OPh)$_3$)$^+$][BF$_4^-$] crystallizes in the centrosymmetric monoclinic space group P2$_1$/n with $a = 12.553(7)$ Å, $b = 16.572(11)$ Å, $c = 15.112(8)$ Å, $\beta = 100.00(4)°$, $V = 3096(3)$ Å^3 and D(calcd.) = 1.579 g/cm^3 for $Z = 4$. The structure was refined to $R(F) = 5.83\%$ for 1972 reflections above $4\sigma(F)$. The cation contains two CpFe(CO) fragments linked *via* an iron—iron bond (Fe(1)—Fe(2) = 2.544(3) Å), a bridging carbonyl ligand (Fe(1)—C(4) = 1.918(1) Å, Fe(2)—C(4) = 1.946(12) Å) and a bridging CHP(OPh)$_3$ ligand (Fe(1)—C(1) = 1.980(9) Å, Fe(2)—C(1) = 1.989(8) Å). Distances within the μ-CHP(OPh)$_3$ moiety include a rather short carbon—phosphorus bond [C(1)—P(1) = 1.680(10) Å] and P—O bond lengths of 1.550(7)–1.579(6) Å. The crystal is stabilized by a network of F···H—C interactions involving the BF$_4^-$ anion.

[Cp$_2$Fe$_2$(CO)$_2$(μ-CO)(μ-CHPPh$_3$)$^+$][BF$_4^-$], which differs from the previous compound only in having a μ-CHPPh$_3$ (rather than μ-CHP(OPh)$_3$) ligand, crystallizes in the centrosymmetric monoclinic space group P2$_1$/c with $a = 11.248(5)$ Å, $b = 13.855(5)$ Å, $c = 18.920(7)$ Å, $\beta = 96.25(3)°$, $V = 2931(2)$ Å^3 and D(calcd.) = 1.559 g/cm^3 for $Z = 4$. This structure was refined to $R(F) = 4.66\%$ for 1985 reflections above $4\sigma(F)$. Bond lengths within the dinuclear cation here include Fe(1)—Fe(2) = 2.529(2) Å, Fe(1)—C(3) = 1.904(9) Å and Fe(2)—C(3) = 1.911(8) Å (for the bridging CO ligand) and Fe(1)—C(1P) = 1.995(6) Å and Fe(2)—C(1P) = 1.981(7) Å (for the bridging CHPPh$_3$ ligand). Distances within the μ-CHPPh$_3$ ligand include a longer carbon—phosphorus bond [C(1P)—P(1) = 1.768(6) Å] and P(1)—C(phenyl) = 1.797(7)–1.815(8) Å.

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Keywords: Organoiron complex; Dinuclear iron complex; Phosphonium ylid; Crystal structure; Hydrogen bonding

INTRODUCTION

Dinuclear organoiron species containing a phosphonium ylid were reported by Pettit and coworkers almost twenty years ago [1]. We have recently reported the crystal structures of two such species, $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPPh_3)^+][PF_6^-]$ [2] and $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPMe_3)^+][PF_6^-]$ [3]. We have now extended these studies to prepare an ylid derived from triphenylphosphite, $P(OPh)_3$. In this paper we report the crystal structure of $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHP(OPh)_3)^+][BF_4^-]$ and of the closely-related triphenylphosphine (PPh_3) analog, $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPPh_3)^+][BF_4^-]$.

EXPERIMENTAL

Synthesis of Dinuclear Iron Ylid Complexes

The synthetic route to these species was analogous to that described previously for the production of $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPPh_3)^+][PF_6^-]$ [1, 2] save that BF_4^- salts were used throughout and the final step involved addition of either $P(OPh)_3$ ($X = OPh$) or PPh_3 ($X = Ph$). The synthetic route may be summarized as follows:

$$\begin{array}{l}
Cp_2Fe_2(CO)_4 \\
\quad\downarrow \; CH_2{=}PPh_3 \\
Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_2) \\
\quad\downarrow \; [Ph_3C^+][BF_4^-] \\
[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH)^+][BF_4^-] \\
\quad\downarrow \; PX_3(X = OPh, Ph) \\
[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPX_3)^+][BF_4^-]
\end{array}$$

The resulting species were recrystallized from dichloromethane/hexanes and characterized by their IR spectra (ν_{C-O} = 1998(s), 1962(m,sh), 1814(m) for the $P(OPh)_3$ derivative; ν_{C-O} = 1992(s), 1955(m), 1809(m) for the PPh_3 derivative) and by single-crystal X-ray diffraction studies.

Collection of X-Ray Diffraction Data, Structural Determination and Refinement for $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHP(OPh)_3)^+][BF_4^-]$

A red parallelepiped of approximate orthogonal dimensions 0.18 × 0.22 × 0.28 mm was carefully sealed into a glass capillary, mounted on a eucentric goniometer and transferred to a Siemens R3m/V diffractometer. Determination of the crystal's Laue symmetry, crystal class and orientation matrix were carried out as described previously [4]. Details are provided in Table I.

Diffraction data were collected and corrected for Lorentz and polarization effects. The systematic absences ($h0\ell$ for $h+\ell=2n+1$ and $0k0$ for

TABLE I Experimental data for the X-ray diffraction studies

Compound	$[Cp_2Fe_2(CO)_2(\mu\text{-}CO)$ $(\mu\text{-}CHP(OPh)_3)^+][BF_4^-]$	$[Cp_2Fe_2(CO)_2(\mu\text{-}CO)$ $(\mu\text{-}CHPPh_3)^+][BF_4^-]$
Formula	$C_{32}H_{26}BF_4Fe_2O_6P$	$C_{32}H_{26}BF_4Fe_2O_3P$
Fw	736.0	688.0
Temperature (K)	296	296
Crystal System	Monoclinic	Monoclinic
Space Group	$P2_1/n$ (No. 14, var)	$P2_1/c$ (No. 14)
a, Å	12.553(7)	11.248(5)
b, Å	16.572(11)	13.855(5)
c, Å	15.112(8)	18.920(7)
β, deg	100.00(4)	96.25(3)
V, Å^3	3096(3)	2931(2)
Z	4	4
D(calc'd), g/cm^3	1.579	1.559
μ(MoKα),mm^{-1}	1.053	1.100
F(000)	1496	1400
Diffractometer	Siemens R3m/V	†
Radiation	Mo Kα ($\lambda=0.71073$ Å)	†
Monochromator	Highly oriented graphite	†
Data collected	$+h, +k, \pm \ell$	$+h, \pm k, \pm \ell$(2 forms)
Scan type	$2\theta-\theta$	$2\theta-\theta$
2θ range, deg	5.0–45.0	6.0–42.0
Scan speed (ω), deg/min	1.50	2.00
Scan range (ω)	$0.6+\Delta(K\alpha_1/K\alpha_2)$	$0.57+\Delta(K\alpha_1/K\alpha_2)$
Absorption correction	N/A	semi-empirical (ψ)
Min/max transmission	N/A	0.5036/0.5795
Reflections collected	4477	6672
Independent reflection	4081 ($R_{int}=3.23\%$)	3152 ($R_{int}=1.49\%$)
Independent reflections with $F_o>4\sigma$	1972	1985
Number of variables	418	388
Extinction correction (χ)	0.00013(5)	N/A
$R(F)$, $R(wF)$ (obs'd data)	5.83%, 4.41%	4.66%, 3.94%
$R(F)$, $R(wF)$ (all data)	10.69%, 5.55%	8.66%, 4.56%
Goodness-of-fit	1.28	1.42
Largest diff. peak, e/Å^3	0.44	0.46
Largest diff. hole, e/Å^3	− 0.38	− 0.52

†Entry same as for previous column.

$k = 2n+1$) uniquely define the centrosymmetric monoclinic space group $P2_1/n$. The 4477 reflections were merged to a set of 4081 unique data ($R(\mathrm{int}) = 3.23\%$) of which 1972 (48.3%) had $|F_o| > 4.0\sigma(|F_o|)$; the data set is clearly rather weak.

All crystallographic calculations were carried out on a VAXstation 3100 computer with use of Siemens SHELXTL PLUS (Release 4.11) VMS program package [5]. The scattering factors used were the analytical values for neutral atoms; these were corrected for both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion [6]. The structure was solved by direct methods. All non-hydrogen atoms were located and their positional and anisotropic thermal parameters were refined. Hydrogen atoms were included in idealized positions, based upon $d(\mathrm{C{-}H}) = 0.96$ Å [7] and the appropriate trigonal or staggered-tetrahedral stereochemistry. Their thermal parameters were refined in blocks, yielding $U = 0.101(14)$ Å^2 for the hydrogen atoms of the Cp rings and $U = 0.058(9)$ Å^2 for the hydrogen atoms of the Ph groups. Refinement was continued until $\Delta/\sigma < 0.01$ for each parameter. A final difference-Fourier synthesis showed no unusual features. The final discrepancy index is $R(F) = 5.83\%$ for those 1972 independent reflections with $|F_o| > 4\sigma$ ($|F_o|$); the value for all 4081 independent data is substantially higher because of the large number of very weak data. Final atomic coordinates are provided in Table II.

Collection of X-Ray Diffraction Data, Structural Determination and Refinement for $[\mathrm{Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPPh_3)^+}][\mathrm{BF_4^-}]$

A red-brown pentagonal plate of approximate dimensions 0.3 × 0.3 × 0.1 mm was sealed into a capillary; experimental details appear in Table I. Important differences from the previous study include the following: (1) The systematic absences ($h0\ell$ for $\ell = 2n+1$ and $0k0$ for $k = 2n+1$) define the standard space group $P2_1/c$. (2) A total of 6672 reflections, representing two equivalent forms, was collected, corrected for absorption and Lp-factors and merged to a set of 3152 unique data ($R(\mathrm{int}) = 1.49\%$) of which 1985 (63.0%) had $|F_o| > 4.0\sigma(|F_o|)$. (3) The final discrepancy index was $R(F) = 4.66\%$ for those 1985 data with $|F_o| > 4.0\sigma(|F_o|)$ and $R(F) = 8.66\%$ for all 3152 unique data. (4) Final atomic parameters are collected in Table III.

Crystal Structure of $[\mathrm{Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHP(OPh)_3)^+}][\mathrm{BF_4^-}]$

Figure 1 shows the packing of $[\mathrm{Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHP(OPh)_3)^+}]$ cations and $\mathrm{BF_4^-}$ anions viewed down '*b*'. The structure is stabilized by an extensive network of weak hydrogen bonds among which are several

TABLE II Final atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHP(OPh)_3)^+][BF_4^-]$

	x	y	z	$U(eq)$
Fe(1)	5762(1)	3080(1)	1816(1)	43(1)
Fe(2)	3741(1)	3346(1)	1393(1)	44(1)
P(1)	4704(2)	3528(2)	3538(2)	44(1)
C(1)	4792(7)	3708(6)	2459(6)	39(4)
C(2)	3163(8)	2553(7)	1876(8)	54(5)
O(2)	2708(6)	2019(5)	2138(5)	82(4)
C(3)	5810(9)	2204(7)	2447(8)	59(5)
O(3)	5924(7)	1596(5)	2829(6)	98(4)
C(4)	4678(8)	2565(7)	947(8)	53(5)
O(4)	4614(6)	2048(5)	422(6)	86(4)
O(5)	3928(5)	4087(4)	3959(4)	54(3)
O(6)	4386(5)	2636(4)	3660(4)	48(3)
O(7)	5783(5)	3635(4)	4240(4)	54(3)
C(11)	7015(16)	2845(11)	1138(22)	139(14)
C(12)	7436(12)	3082(17)	2001(17)	133(12)
C(13)	7097(13)	3846(12)	2086(10)	79(7)
C(14)	6512(10)	4079(8)	1310(13)	69(6)
C(15)	6458(12)	3467(14)	725(9)	94(8)
C(21)	3117(10)	4527(7)	1173(8)	58(5)
C(22)	2298(9)	3975(8)	1143(9)	61(5)
C(23)	2350(9)	3470(8)	409(9)	68(5)
C(24)	3258(10)	3686(8)	33(8)	71(6)
C(25)	3722(9)	4355(7)	522(9)	58(5)
C(51)	2810(9)	4199(7)	3661(7)	48(5)
C(52)	2109(9)	3580(7)	3649(7)	55(5)
C(53)	1021(10)	3731(8)	3433(8)	69(6)
C(54)	673(10)	4482(10)	3169(8)	68(6)
C(55)	1385(10)	5104(8)	3137(7)	66(5)
C(56)	2469(9)	4951(7)	3386(7)	55(5)
C(61)	4368(7)	2177(6)	4446(8)	37(4)
C(62)	4666(8)	2455(7)	5301(9)	53(5)
C(63)	4635(7)	1941(9)	5998(7)	55(5)
C(64)	4342(9)	1159(8)	5853(9)	62(6)
C(65)	4076(9)	879(8)	4994(9)	67(6)
C(66)	4072(9)	1388(7)	4279(8)	61(5)
C(71)	6561(8)	4256(7)	4240(7)	45(5)
C(72)	7613(9)	4019(7)	4500(7)	57(5)
C(73)	8413(9)	4578(8)	4478(7)	59(5)
C(74)	8157(9)	5349(8)	4242(8)	64(6)
C(75)	7098(11)	5573(7)	3999(8)	72(6)
C(76)	6285(9)	5024(7)	3997(7)	57(5)
B(1)	4952(16)	6348(12)	1934(13)	85(9)
F(1)	5251(7)	5750(5)	1506(8)	169(6)
F(2)	5697(7)	6925(6)	2063(7)	170(5)
F(3)	4663(7)	6161(6)	2709(7)	161(5)
F(4)	4052(9)	6694(6)	1428(6)	165(5)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

F···H—C bonds (involving the BF_4^- anions) and O···H—C bonds (involving the μ-CO ligand). Figure 2 shows the labelling of atoms within the dinuclear cation. Interatomic distances and angles are collected in Tables IV and V. The two iron atoms are linked by a direct metal–metal bond

TABLE III Final atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $[CP_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPPh_3)^+][BF_4^-]$

	x	*y*	*z*	*U*(*eq*)
Fe(1)	7500(1)	6562(1)	6777(1)	51(1)
Fe(2)	8274(1)	4914(1)	6478(1)	44(1)
P(1)	7249(2)	5055(1)	8120(1)	39(1)
C(1P)	7197(6)	5276(4)	7196(3)	39(3)
O(1)	9514(6)	7326(5)	7671(3)	101(3)
C(1)	8683(9)	6978(6)	7354(4)	67(4)
O(2)	10514(5)	4840(5)	7379(3)	86(3)
C(2)	9600(8)	4877(6)	7046(4)	53(3)
O(3)	9387(5)	6538(4)	5837(3)	77(3)
C(3)	8698(8)	6182(6)	6195(4)	56(4)
C(11)	5720(13)	6668(11)	6317(13)	143(9)
C(12)	5893(13)	7239(12)	6928(6)	94(6)
C(13)	6695(14)	7901(8)	6846(8)	105(7)
C(14)	7047(15)	7788(13)	6184(11)	161(10)
C(15)	6457(24)	7050(17)	5876(9)	190(14)
C(21)	7966(11)	4678(6)	5361(4)	72(4)
C(22)	8910(9)	4114(7)	5658(5)	74(4)
C(23)	8439(10)	3492(6)	6153(4)	71(4)
C(24)	7225(10)	3686(6)	6152(4)	65(4)
C(25)	6948(9)	4432(7)	5668(5)	69(4)
C(31)	8454(7)	5622(6)	8670(3)	41(3)
C(32)	9492(8)	5096(6)	8865(4)	60(3)
C(33)	10429(10)	5500(9)	9295(5)	90(5)
C(34)	10316(11)	6410(9)	9549(5)	92(5)
C(35)	9309(11)	6944(7)	9372(5)	78(4)
C(36)	8370(8)	6554(6)	8911(4)	60(3)
C(41)	7336(6)	3797(5)	8363(3)	35(3)
C(42)	6881(6)	3485(6)	8974(4)	54(3)
C(43)	6985(7)	2530(6)	9199(4)	62(4)
C(44)	7525(7)	1896(6)	8805(5)	64(4)
C(45)	7987(8)	2175(6)	8195(5)	75(4)
C(46)	7901(8)	3134(6)	7986(4)	64(4)
C(51)	5865(7)	5461(5)	8432(4)	47(3)
C(52)	5819(8)	5864(6)	9096(5)	79(4)
C(53)	4739(12)	6125(8)	9319(7)	113(6)
C(54)	3704(12)	5987(8)	8892(8)	114(7)
C(55)	3718(9)	5561(7)	8260(6)	89(5)
C(56)	4802(8)	5286(6)	8022(5)	63(4)
B(1)	6310(17)	6030(15)	3786(8)	115(8)
F(2)	5875(6)	5286(5)	4062(5)	191(4)
F(3)	7196(10)	5765(8)	3488(7)	268(8)
F(4)	5602(7)	6565(5)	3383(4)	174(4)
F(1)	6791(15)	6499(6)	4305(5)	323(9)

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

(Fe(1)—Fe(2) = 2.544(3) Å), by a bridging carbonyl ligand (Fe(1)—C(4) = 1.918(10) Å and Fe(2)—C(4) = 1.946(12) Å) and by a bridging $CHP(OPh)_3$ ligand (Fe(1)—C(1) = 1.980(9) Å and Fe(2)—C(1) = 1.989(8) Å). The bridging carbonyl ligand is located symmetrically, as indicated by the angles Fe(1)—C(4)—O(4) = 138.8(9)° and Fe(2)—C(4)—O(4) = 138.9(8)°.

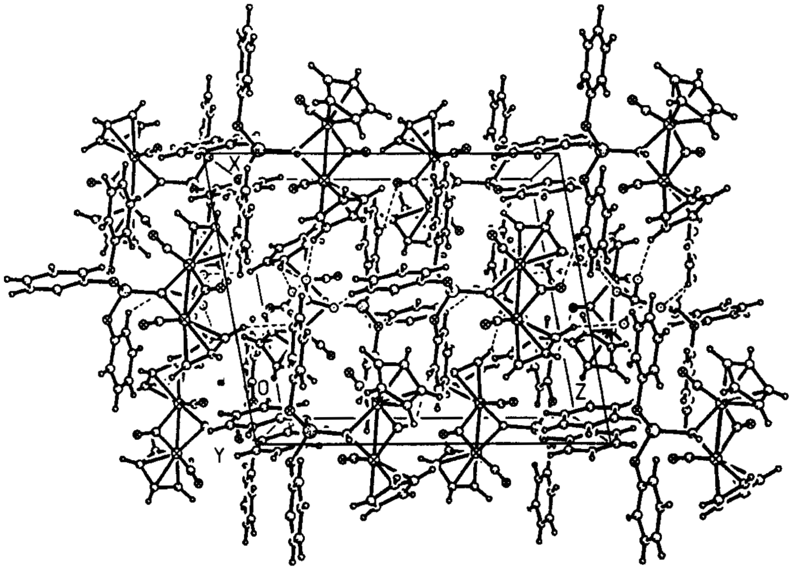

FIGURE 1 Packing diagram for $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHP(OPh)_3)^+][BF_4^-]$, viewed down '*b*'; the *c*-axis is horizontal and the *a*-axis some 10° from vertical. Iron and oxygen atoms are identified by a cross, phosphorus atoms are shaded and fluorine atoms have a central dot. Note the F···H—C and (μ-C—O)···H—C interactions.

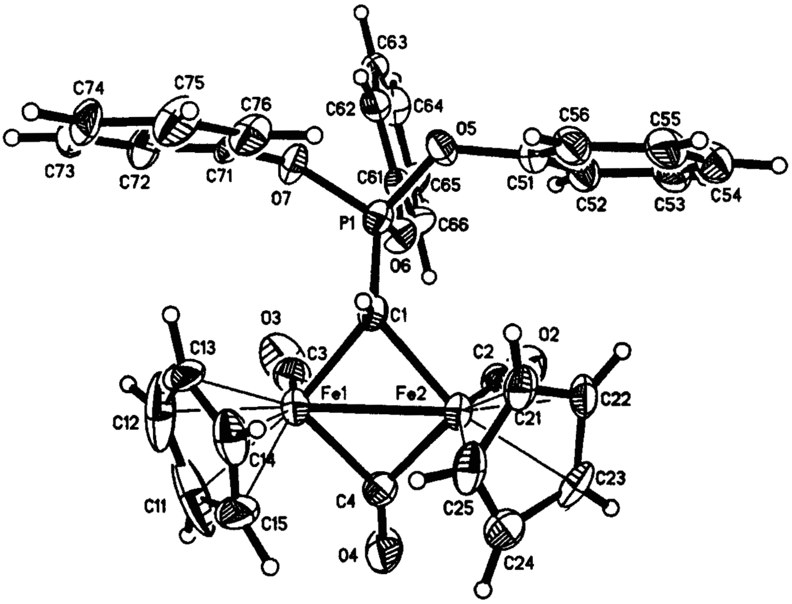

FIGURE 2 Labelling of atoms in the $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHP(OPh)_3)^+]$ cation; with 30% probability envelopes for non-hydrogen atoms and with hydrogen atoms artificially reduced.

TABLE IV Interatomic distances (Å) for $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHP(OPh)_3)^+][BF_4^-]$

(A) Iron—Iron bond			
Fe(1)—Fe(2)			
(B) Iron—ligand distances			
Fe(1)—C(1)	1.980(9)	Fe(2)—C(1)	1.989(8)
Fe(1)—C(3)	1.732(12)	Fe(2)—C(2)	1.723(12)
Fe(1)—C(4)	1.918(10)	Fe(2)—C(4)	1.946(12)
Fe(1)—C(11)	2.059(27)	Fe(2)—C(21)	2.113(12)
Fe(1)—C(12)	2.072(15)	Fe(2)—C(22)	2.067(12)
Fe(1)—C(13)	2.086(17)	Fe(2)—C(23)	2.098(11)
Fe(1)—C(14)	2.114(15)	Fe(2)—C(24)	2.117(12)
Fe(1)—C(15)	2.095(16)	Fe(2)—C(25)	2.126(13)
(C) P—C and P—O distances			
P(1)—C(1)	1.680(10)	P(1)—O(6)	1.550(7)
P(1)—O(5)	1.557(8)	P(1)—O(7)	1.579(6)
(D) C—O distances			
C(2)—O(2)	1.160(14)	O(5)—C(51)	1.410(12)
C(3)—O(3)	1.158(15)	O(6)—C(61)	1.414(13)
C(4)—O(4)	1.162(14)	O(7)—C(71)	1.418(13)
(E) C—C distances within Cp ligands			
C(11)—C(12)	1.377(38)	C(21)—C(22)	1.371(17)
C(12)—C(13)	1.350(33)	C(22)—C(23)	1.400(19)
C(13)—C(14)	1.328(23)	C(23)—C(24)	1.405(19)
C(14)—C(15)	1.339(26)	C(24)—C(25)	1.402(18)
C(15)—C(11)	1.339(28)	C(25)—C(21)	1.373(19)
(F) C—C distances within phenyl rings			
C(51)—C(52)	1.350(16)	C(61)—C(62)	1.362(17)
C(52)—C(53)	1.371(16)	C(62)—C(63)	1.360(18)
C(53)—C(54)	1.356(20)	C(63)—C(64)	1.355(19)
C(54)—C(55)	1.371(19)	C(64)—C(65)	1.365(19)
C(55)—C(56)	1.371(16)	C(65)—C(66)	1.369(18)
C(56)—C(51)	1.358(17)	C(66)—C(61)	1.371(16)
C(71)—C(72)	1.368(15)	C(74)—C(75)	1.368(17)
C(72)—C(73)	1.371(17)	C(75)—C(76)	1.366(17)
C(73)—C(74)	1.350(18)	C(76)—C(71)	1.353(16)
(G) B—F distances			
B(1)—F(1)	1.274(23)	B(1)—F(3)	1.321(24)
B(1)—F(2)	1.328(22)	B(1)—F(4)	1.376(21)

The ylid ligand is in a slightly asymmetric environment, with ∠Fe(1)—C(1)—P(1) = 122.2(5)° and ∠Fe(2)—C(1)—P(1) = 125.8(5)° (difference = 3.6°); this is of little energetic significance and is probably a result of intermolecular interactions: The two terminal iron—carbonyl distances are Fe(1)—C(3) = 1.732(12) Å and Fe(2)—C(2) = 1.723(12) Å; these two ligands are slightly distorted from linearity (∠Fe(1)—C(3)—O(3) = 173.4(11)° and ∠Fe(2)—C(2)—O(2) = 174.4(9)°),

TABLE V Interatomic angles (°) for $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHP(OPh)_3)^+][BF_4^-]$

(A) Angles around the iron atoms			
Fe(2)—Fe(1)—C(1)	50.3(2)	Fe(1)—Fe(2)—C(1)	50.0(3)
Fe(2)—Fe(1)—C(3)	102.8(4)	Fe(1)—Fe(2)—C(2)	103.7(3)
Fe(2)—Fe(1)—C(4)	49.3(3)	Fe(1)—Fe(2)—C(4)	48.4(3)
C(1)—Fe(1)—C(3)	97.8(5)	C(1)—Fe(2)—C(2)	99.0(4)
C(1)—Fe(1)—C(4)	98.4(4)	C(1)—Fe(2)—C(4)	97.2(4)
C(3)—Fe(1)—C(4)	87.5(5)	C(2)—Fe(2)—C(4)	87.9(5)
(B) Angles associated with the ylid core			
C(1)—P(1)—O(5)	116.2(4)	O(5)—P(1)—O(6)	109.0(4)
C(1)—P(1)—O(6)	110.3(4)	O(5)—P(1)—O(7)	100.5(4)
C(1)—P(1)—O(7)	116.0(4)	O(6)—P(1)—O(7)	103.6(4)
Fe(1)—C(1)—P(1)	122.2(5)	P(1)—O(5)—C(51)	127.3(6)
Fe(2)—C(1)—P(1)	125.8(5)	P(1)—O(6)—C(61)	130.9(6)
Fe(1)—C(1)—Fe(2)	79.7(3)	P(1)—O(7)—C(71)	126.3(6)
(C) Angles associated with carbonyl ligands			
Fe(1)—C(3)—O(3)	173.4(11)	Fe(2)—C(2)—O(2)	174.4(9)
Fe(1)—C(4)—O(4)	138.8(9)	Fe(2)—C(4)—O(4)	138.9(8)
Fe(1)—C(4)—Fe(2)	82.3(5)		
(D) Angles within Cp ligands			
C(15)—C(11)—C(12)	107.8(20)	C(25)—C(21)—C(22)	110.0(11)
C(11)—C(12)—C(13)	106.4(18)	C(21)—C(22)—C(23)	106.7(11)
C(12)—C(13)—C(14)	108.9(16)	C(22)—C(23)—C(24)	108.7(11)
C(13)—C(14)—C(15)	108.6(14)	C(23)—C(24)—C(25)	106.2(12)
C(14)—C(15)—C(11)	108.3(17)	C(24)—C(25)—C(21)	108.2(11)
(E) O—C—C(phenyl) angles			
O(5)—C(51)—C(52)	120.9(10)	O(5)—C(51)—C(56)	117.6(10)
O(6)—C(61)—C(62)	125.0(9)	O(6)—C(61)—C(66)	113.7(9)
O(7)—C(71)—C(72)	115.0(10)	O(7)—C(71)—C(76)	122.6(9)
(F) C—C—C(phenyl) angles			
C(56)—C(51)—C(52)	121.5(10)	C(66)—C(61)—C(62)	121.2(11)
C(51)—C(52)—C(53)	119.0(11)	C(61)—C(62)—C(63)	118.9(11)
C(52)—C(53)—C(54)	119.7(12)	C(62)—C(63)—C(64)	121.2(11)
C(53)—C(54)—C(55)	121.4(11)	C(63)—C(64)—C(65)	119.6(12)
C(54)—C(55)—C(56)	118.3(12)	C(64)—C(65)—C(66)	120.6(12)
C(55)—C(56)—C(51)	119.1(11)	C(65)—C(66)—C(61)	118.6(11)
C(76)—C(71)—C(72)	122.5(11)	C(73)—C(74)—C(75)	120.2(11)
C(71)—C(72)—C(73)	118.3(11)	C(74)—C(75)—C(76)	120.7(11)
C(72)—C(73)—C(74)	120.2(10)	C(75)—C(76)—C(71)	118.0(10)
(G) F—B—F angles within BF_4^- anion			
F(1)—B(1)—F(2)	111.8(16)	F(2)—B(1)—F(3)	109.5(15)
F(1)—B(1)—F(3)	114.7(17)	F(2)—B(1)—F(4)	105.7(15)
F(1)—B(1)—F(4)	109.1(15)	F(3)—B(1)—F(4)	105.4(15)

probably as a result of repulsion between C(2) and C(3)(which occupy an eclipsed conformation about the Fe(1)—Fe(2) bond). A similar phenomenon occurs in *cis*-$Cp_2Fe_2(CO)_2$ $(\mu\text{-}CO)_2$ (but not the *trans*-isomer) [8, 9].

Fe-C(Cp) distances range from 2.059(27)Å to 2.114(15)Å (averaging 2.085Å) for Fe(1) and from 2.067(12)Å to 2.126(13)Å (averaging 2.104Å) for Fe(2). Carbon-carbon distances within the Cp rings are reduced systematically as a result of libration. Those in the ring defined by atoms C(11)→C(15), which undergoes a larger amplitude of librational motion, provide C—C bond lengths of 1.328(23)Å→ 1.377(38)Å, averaging 1.339Å; atoms C(21)→C(25) are associated with C—C distances of 1.355(19)Å→ 1.371(16)Å, averaging 1.364Å. [This aspect is discussed in greater detail in the context of the second structural study, *vide infra.*] The ylid fragment is associated with an unusually short C—P bond (C(1)—P(1) = 1.680(10)Å) and with P—O distances of 1.550(7)Å→ 1.579(6)Å (averaging 1.562Å). The C—P—O angles are all greater than the ideal tetrahedral value (C(1)—P(1)—O(5) = 116.2(4)°, C(1)—P(1)—O(6) = 110.3(4)° and C(1)—P(1)—O(7) = 116.0(4)°), while the O—P—O angles are, in general, reduced from this value (O(5)—P(1)—O(6) = 109.0(4)°, O(5)—P(1)—O(7) = 100.5(4)° and O(6)—P(1)—O(7) = 103.6(4)°). The P—O—C angles are all quite obtuse, with values in the range 126.3(6)°→ 130.9(6)°.

Finally we note that the phenyl rings are well defined and that the internal angles at the *ipso* carbons are all expanded slightly from the ideal trigonal value (*viz.*, C(56)—C(51)—C(52) = 121.5(10)°, C(66)—C(61)—C(62) = 121.2(11)°, C(76)—C(71)—C(72) = 122.5(11)°), averaging 121.7°.

Crystal Structure of [$Cp_2Fe_2(CO)_2(\mu$-CO)(μ-CHPPh$_3)^+$][BF_4^-]

Figure 3 shows the packing of [$Cp_2Fe_2(CO)_2$ (μ-CO)(μ-CHPPh$_3)^+$] cations and BF_4^- anions. Once again, there are a number of weak F···C—H hydrogen bonds involving the BF_4^- anions. The labelling of atoms is illustrated in Figure 4, while interatomic distances and angles are collected in Tables VI and VII. The structure of the cation is very similar to that observed in [$Cp_2Fe_2(CO)_2(\mu$-CO)(μ-CHPPh$_3)^+$][PF_6^-] [2] and the overall structure resembles that of [$Cp_2Fe_2(CO)_2(\mu$-CO)(μ-CHP(OPh)$_3)^+$][BF_4^-], described above. Details of interest include the following.

(1) The metal-metal bond, Fe(1)—Fe(2) = 2.529(2)Å, is essentially identical to the value of 2.530(1)Å in the corresponding [PF_6^-] derivative [2] and is significantly reduced from the value of 2.544(3)Å found in the analogous μ-CHP(OPh)$_3$ complex (*vide supra*).

(2) The bridging carbonyl ligand is situated symmetrically, with Fe(1)—C(3) = 1.904(9)Å, Fe(2)—C(3) = 1.911(8)Å, ∠Fe(1)—C(3)—O(3) = 139.5(7)° and ∠Fe(2)—C(3)—O(3) = 137.5(7)°.

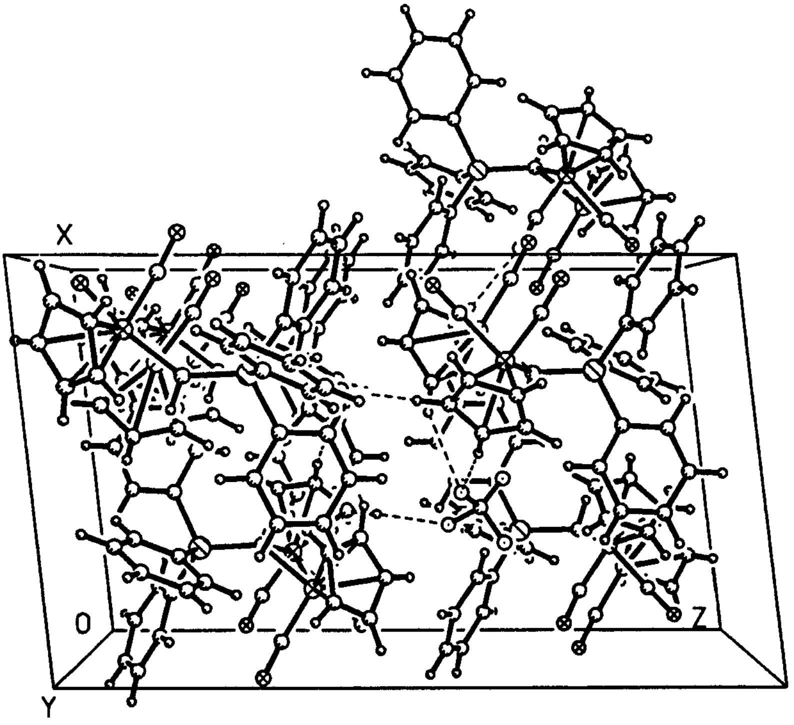

FIGURE 3 Packing diagram for $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPPh_3)^+][BF_4^-]$, with atoms identified as in Figure 1. The cell is viewed down '*b*' with the *c*-axis horizontal and the *a*-axis some 6° (*i.e.*, *β*-90°) from the vertical.

(3) The $CHPPh_3$ ligand is associated with distances of Fe(1)—C(1P) = 1.995(6) Å and Fe(2)—C(1P) = 1.981(7) Å, but is rather asymmetrically located, with angles of Fe(1)—C(1P)—P(1) = 124.0(3)° and Fe(2)—C(1P)—P(1) = 132.6(4)° (*cf.* inequivalent angles of 123.8(4)° and 130.2(3)° for the $[PF_6^-]$ salt [2]).

(4) The two eclipsed terminal carbonyl ligands are again bent, due to C···C and O···O repulsions, with ∠Fe(1)—C(1)—O(1) = 171.5(8)° and ∠Fe(2)—C(2)—O(2) = 175.2(7)°.

(5) The two ^{5}-cyclopentadienyl rings are clearly undergoing different degrees of torsional thermal motion (libration). This can clearly be seen from electron-density maps through the five-membered rings. See Figures 5a and 5b, where the electron-density defining atoms C(11)—C(15) is far more diffuse than that defining atoms C(21)—C(25). The effect is seen most clearly in the numerical values of thermal parameters ($U_{eq} = 0.094(6) \rightarrow 0.190(14)$ Å^2 for atoms C(11)—C(15), with a maximum

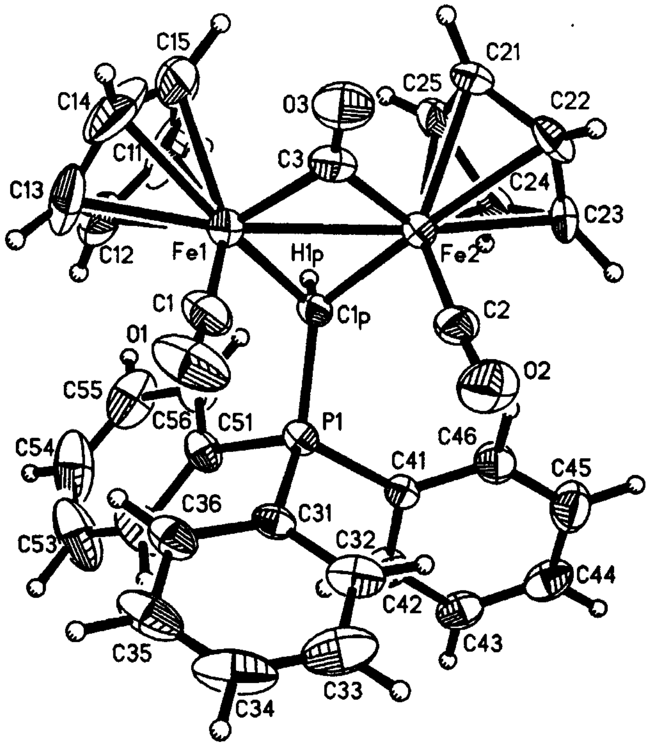

FIGURE 4 Labelling diagram for the $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPPh_3)^+]$ cation; 30% probability envelopes for non-hydrogen atoms, with hydrogen atoms artificially reduced.

diagonal value of $U_{11} = 0.297(32)\,\text{Å}^2$ for C(15); $U_{eq} = 0.065(4) \rightarrow 0.074(4)\,\text{Å}^2$ for C(21)—C(25), with a maximum diagonal value of $0.116(9)\,\text{Å}^2$ for the U_{11} value of C(21)). Iron—carbon distances show some differences and range from 2.069(19) Å→2.099(16) Å (averaging 2.080 Å) for Fe(1) and 2.078(9) Å→2.129(8) Å (averaging 2.110 Å) for Fe(2). C—C(Cp) bond distances are 1.306(21)→1.396(26) Å (average = 1.347 Å) for "ring 1", consisting of atoms C(11)—C(15) and 1.380(16)→1.418(13) Å (average = 1.394 Å) for "ring 2", consisting of atoms C(21)—C(25). Clearly, librational effects are producing an artificial shortening of apparent C—C "bond lengths" in both rings (*cf.* the accepted value of ~ 1.43 Å). The artificial contraction is, however, far more apparent in "ring 1". The Fe—C(Cp) bonds also seem to be affected, but to a smaller degree.

(6) The ylid fragment is centered on the bond P(1)—C(1P) = 1.768(6) Å; this is equivalent to ylid bonds in other species derived from phosphines,

TABLE VI Interatomic distances (Å) for $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPPh_3)^+][BF_4^-]$

(A) Iron—iron bond			
Fe(1)—Fe(2)	2.529(2)		
(B) Iron—ligand distances			
Fe(1)—C(1P)	1.995(6)	Fe(2)—C(1P)	1.981(7)
Fe(1)—C(1)	1.726(9)	Fe(2)—C(2)	1.741(8)
Fe(1)—C(3)	1.904(9)	Fe(2)—C(3)	1.911(8)
Fe(1)—C(11)	2.099(16)	Fe(2)—C(21)	2.129(8)
Fe(1)—C(12)	2.083(15)	Fe(2)—C(22)	2.095(10)
Fe(1)—C(13)	2.075(12)	Fe(2)—C(23)	2.078(9)
Fe(1)—C(14)	2.069(19)	Fe(2)—C(24)	2.124(9)
Fe(1)—C(15)	2.075(20)	Fe(2)—C(25)	2.126(9)
(C) P—C distances			
P(1)—C(1P)	1.768(6)	P(1)—C(41)	1.802(7)
P(1)—C(31)	1.797(7)	P(1)—C(51)	1.815(8)
(D) C—O distances			
C(1)—O(1)	1.160(11)	C(3)—O(3)	1.191(10)
C(2)—O(2)	1.148(10)		
(E) C—C distances within Cp ligands			
C(11)—C(12)	1.396(26)	C(21)—C(22)	1.387(14)
C(12)—C(13)	1.306(21)	C(22)—C(23)	1.418(13)
C(13)—C(14)	1.364(26)	C(23)—C(24)	1.392(15)
C(14)—C(15)	1.320(29)	C(24)—C(25)	1.394(12)
C(15)—C(11)	1.347(31)	C(25)—C(21)	1.380(16)
(F) C—C distances within phenyl groups			
C(31)—C(32)	1.392(12)	C(41)—C(42)	1.385(10)
C(32)—C(33)	1.379(13)	C(42)—C(43)	1.390(12)
C(33)—C(34)	1.361(17)	C(43)—C(44)	1.340(12)
C(34)—C(35)	1.363(16)	C(44)—C(45)	1.372(13)
C(35)—C(36)	1.402(13)	C(45)—C(46)	1.387(12)
C(36)—C(31)	1.376(11)	C(46)—C(41)	1.362(11)
C(51)—C(52)	1.380(12)	C(54)—C(55)	1.335(19)
C(52)—C(53)	1.377(17)	C(55)—C(56)	1.398(14)
C(53)—C(54)	1.356(18)	C(56)—C(51)	1.375(11)
(G) B—F distances			
B(1)—F(1)	1.251(20)	B(1)—F(3)	1.252(22)
B(1)—F(2)	1.276(21)	B(1)—F(4)	1.278(19)

i.e., 1.781(6) Å in $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPPh_3)^+][PF_6^-]$[2] and 1.760(15) Å in $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPMe_3)^+][PF_6^-]$[3], but these bonds are all substantially longer than that of 1.680(10) Å found in the phosphite species, $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHP(OPh)_3)^+][PF_6^-]$, described above.

(7) The P—C(phenyl) distances are in the expected range (1.797(7) Å → 1.815(8) Å); the C(1P)—P(1)—C(*ipso*) angles are generally expanded from the regular tetrahedral value, with individual values of 116.0(3)°,

TABLE VII Interatomic angles (Å) for $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPPh_3)^+][BF_4^-]$

(A) Angles around the iron atoms			
Fe(2)—Fe(1)—C(1P)	50.3(2)	Fe(1)—Fe(2)—C(1P)	50.7(2)
Fe(2)—Fe(1)—C(1)	100.5(3)	Fe(1)—Fe(2)—C(2)	100.4(3)
Fe(2)—Fe(1)—C(3)	48.6(2)	Fe(1)—Fe(2)—C(3)	48.4(3)
C(1P)—Fe(1)—C(1)	101.5(3)	C(1P)—Fe(2)—C(2)	97.5(3)
C(1P)—Fe(1)—C(3)	98.3(3)	C(1P)—Fe(2)—C(3)	98.6(3)
(B) Angles associated with the ylid core			
C(1P)—P(1)—C(31)	116.0(3)	C(31)—P(1)—C(41)	105.0(3)
C(1P)—P(1)—C(41)	114.5(3)	C(31)—P(1)—C(51)	107.2(3)
C(1P)—P(1)—C(51)	109.3(3)	C(41)—P(1)—C(51)	104.0(3)
Fe(1)—C(1P)—P(1)	124.0(3)	Fe(1)—C(1P)—Fe(2)	79.0(2)
Fe(2)—C(1P)—P(1)	132.6(4)		
(C) Angles associated with carbonyl ligands			
Fe(1)—C(1)—O(1)	171.5(8)	Fe(2)—C(2)—O(2)	175.2(7)
Fe(1)—C(3)—O(3)	139.5(7)	Fe(2)—C(3)—O(3)	137.5(7)
Fe(1)—C(3)—Fe(2)	83.0(3)		
(D) Angles within Cp rings			
C(15)—C(11)—C(12)	104.5(15)	C(25)—C(21)—C(22)	109.0(8)
C(11)—C(12)—C(13)	109.6(14)	C(21)—C(22)—C(23)	106.5(9)
C(12)—C(13)—C(14)	107.5(13)	C(22)—C(23)—C(24)	108.6(8)
C(13)—C(14)—C(15)	108.2(17)	C(23)—C(24)—C(25)	107.0(9)
C(14)—C(15)—C(11)	110.1(18)	C(24)—C(25)—C(21)	108.9(9)
(E) P—C—C angles			
P(1)—C(31)—C(32)	118.8(6)	P(1)—C(31)—C(36)	121.9(6)
P(1)—C(41)—C(42)	120.1(5)	P(1)—C(41)—C(46)	122.3(6)
P(1)—C(51)—C(52)	122.7(6)	P(1)—C(51)—C(56)	119.0(6)
(F) C—C—C angles in phenyl rings			
C(36)—C(31)—C(32)	119.3(7)	C(46)—C(41)—C(42)	117.5(7)
C(31)—C(32)—C(33)	120.6(8)	C(41)—C(42)—C(43)	121.8(7)
C(32)—C(33)—C(34)	119.4(10)	C(42)—C(43)—C(44)	118.9(8)
C(33)—C(34)—C(35)	121.5(10)	C(43)—C(44)—C(45)	121.3(8)
C(34)—C(35)—C(36)	119.6(9)	C(44)—C(45)—C(46)	119.2(8)
C(35)—C(36)—C(31)	119.6(8)	C(45)—C(46)—C(41)	121.3(7)
C(56)—C(51)—C(52)	118.0(8)	C(53)—C(54)—C(55)	120.1(12)
C(51)—C(52)—C(53)	120.4(12)	C(54)—C(55)—C(56)	120.3(10)
C(52)—C(53)—C(54)	120.7(11)	C(55)—C(56)—C(51)	120.3(8)
(G) F—B—F angles within BF_4^- anion			
F(1)—B(1)—F(2)	104.5(13)	F(2)—B(1)—F(3)	107.9(16)
F(1)—B(1)—F(3)	102.0(16)	F(2)—B(1)—F(4)	118.1(15)
F(1)—B(1)—F(4)	110.8(16)	F(3)—B(1)—F(4)	112.1(14)

114.5(3)° and 109.3(3)° (average = 113.3°); the C—P—C angles are consistently reduced from 109.5° with values of 104.0(3)°, 105.0(3)° and 107.2(3)° (average = 105.4°). Finally we note that the *ipso* carbon atoms of the phenyl rings are all reduced from the ideal trigonal value, with ∠C(36)—C(31)—C(32) = 119.3(7)°, ∠C(46)—C(41)—C(42) =

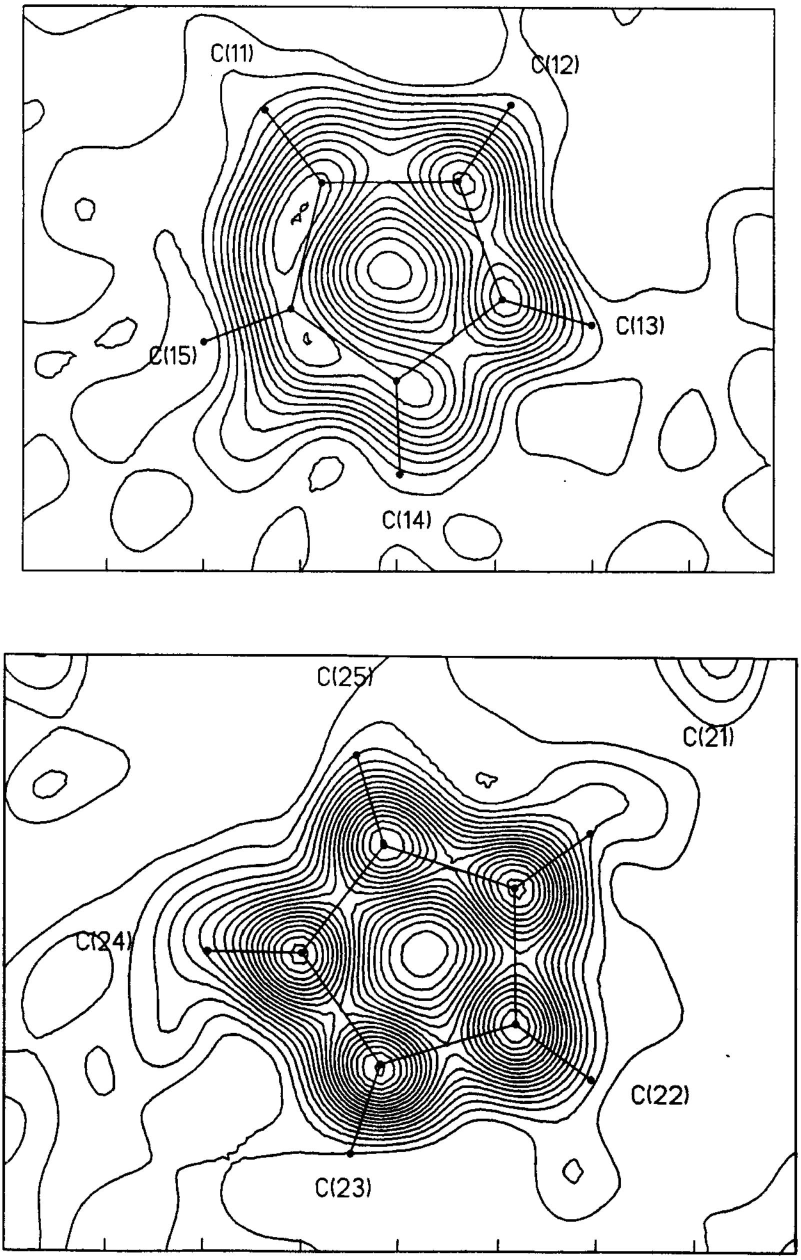

FIGURE 5 Electron-density maps for the η^5-cyclopentadienyl rings in $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHPPh_3)^+][BF_4^-]$. In each case the components ΔF were calculated by omitting atoms from that particular ring. Contours are at intervals of $0.2e^-/Å^3$ starting at the zero contour. (a) Electron-density map for the ring defined by atoms C(11)—C(15); note the diffuse nature of the electron density. (b) A similar diagram for atoms C(21)—C(25); note the better definition of the electron density, particularly near the locations of carbon atoms.

117.5(7)° and ∠C(56)—C(51)—C(52) = 118.0(8)° (average = 118.3°). This is precisely opposite to the pattern observed for the $CHP(OPh)_3$ system above and is a result of the *ipso* carbon atoms being linked to phosphorus, a much less electronegative element than oxygen [10].

CONCLUSIONS

We have extended our range of structural studies on $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHP(X)_3{}^+]$ to include an ylid complex derived from triphenylphosphite. The μ-$CHP(OPh)_3$ ligand has an ylid (CH—P) linkage that is shorter by ~0.1 Å (and is presumably stronger) than those observed in analogous μ-$CHPPh_3$ or μ-$CHPMe_3$ derivatives [2, 3].

Supplementary Material

Additional tabular material for the X-ray diffraction studies is available upon request from M.R.C.

Acknowledgement

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