Structure of a Stable Iron(0) Mono-olefin Chelate Complex with 2-Vinylphenyldiphenylphosphine: Dicarbonylbis[(2-vinylphenyl)diphenylphosphine]iron(0)

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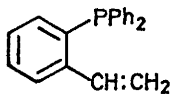
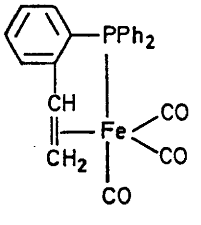
The crystal and molecular structure of the title compound, a mono-olefin analogue of $Fe(CO)_5$, has been determined from three-dimensional *X*-ray diffractometer data. Atom parameters have been refined in the non-standard centred space group $B2_1/c$ [monoclinic, $a = 15{\cdot}771(6)$, $b = 18{\cdot}468(6)$, $c = 24{\cdot}499(8)$ Å, $\beta = 97{\cdot}76(3)°$, $Z = 8$]. Block-diagonal least-squares refinement has converged at R 0·050 for 2776 unique reflections. The ligand arrangement is approximately trigonal bipyramidal about the central iron atom, with phosphorus atoms in the axial sites; the equatorial sites are occupied by one π-bonded vinyl and two carbonyl groups. Fe–P in the chelated sp ligand [2·205(2) Å] is significantly shorter than that in the unidentate ligand [2·239(2) Å]. The π-bonded vinyl group is symmetrically co-ordinated, with Fe–C 2·092(5) and 2·108(5) Å.

IN general, mono-olefin substituted derivatives of $Fe(CO)_5$, *e.g.*, $Fe(CO)_4(CH_2{:}CH_2)$, are thermally unstable and air-sensitive,[1,2] while the analogous ruthenium derivatives are unknown. If, however, the double bond carries a strong electron-withdrawing group, the complexes appear to be more stable.[3,4] Such a requirement is met by the potentially bidentate ligand (2-vinylphenyl)diphenylphosphine [sp, o-$CH_2{:}CH{\cdot}C_6H_4{\cdot}PPh_2$, (I)] which, as discussed elsewhere,[5] serves not only to stabilize mono-olefin iron(0) complexes, but also their ruthenium analogues.

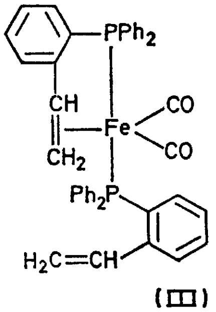


(I)

In particular, the reaction of sp with freshly prepared $Fe_3(CO)_{12}$ when heated under reflux in n-octane gives two air-stable products of empirical formula $Fe(CO)_3(sp)$ (II) and $Fe(CO)_2(sp)_2$ (III). The analogous ruthenium complexes $Ru(CO)_3(sp)$ and $Ru(CO)_2(sp)_2$ are obtained similarly from $Ru_3(CO)_{12}$.



(II)



(III)

I.r. and n.m.r. data suggest the structural assignments (II) and (III) for the mono- and bis-phosphine derivatives respectively. Assignment (III) is confirmed by the present single-crystal analysis of $Fe(CO)_2(sp)_2$; Debye–Scherrer photographs show $Ru(CO)_2(sp)_2$ to be isomorphous and probably isostructural. We now report, in detail, the structure of $Fe(CO)_2(sp)_2$; a preliminary account of this work has appeared elsewhere.[5]

EXPERIMENTAL

Crystal Data.—$C_{42}H_{34}FeO_2P_2$, $M = 688{\cdot}5$, Monoclinic, $a = 15{\cdot}771(6)$, $b = 18{\cdot}468(6)$, $c = 24{\cdot}499(8)$ Å, $\beta = 97{\cdot}76(3)°$, $U = 7070{\cdot}4$ Å^3, $D_m = 1{\cdot}28(1)$, $Z = 8$, $D_c = 1{\cdot}29$, $F(000) = 2864$. Space group $B2_1/c$, Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 45{\cdot}39$ cm^{-1}.

Systematic absences define the space group $P2_1/c$ with $a' = 13{\cdot}644$, $b' = 18{\cdot}468$, $c' = 24{\cdot}499$ Å, $\beta' = 145{\cdot}06°$. Atom parameters have been refined and tabulated for the non-standard space group $B2_1/c$, for which the equipoints are: (x,y,z); $(x + \frac{1}{2},y,z + \frac{1}{2})$; $(\bar{x},\bar{y},\bar{z})$; $(\frac{1}{2} - x,\bar{y},\frac{1}{2} - z)$; $(x,\frac{1}{2} - y,\frac{1}{2} + z)$; $(\frac{1}{2} + x,\frac{1}{2} - y,z)$; $(\bar{x},\frac{1}{2} + y,\frac{1}{2} - z)$; $(\frac{1}{2} - x,\frac{1}{2} + y,\bar{z})$. Space group $B2_1/c$ is a non-standard form of $P2_1/c$ (C_{2h}^5, No. 14), and was chosen because of the associated β angle. The crystal chosen for data collection, of dimension 0·02 × 0·008 × 0·008 cm (elongated in the *a* direction) was transferred to a Picker FACS-I automatic diffractometer, and aligned with the crystallographic *a*- and machine Φ-axes approximately coincidental. Cell dimensions and crystal orientation matrix, together with estimated standard errors, were obtained in the usual way from least-squares refinement of the 2θ, ω, X, and Φ values of 12 carefully centred high-angle reflections. Busing and Levy programs[6] were used for all phases of diffractometer control and data collection.

Data Collection.—Including standards, 4650 reflections of the form *hkl* and *hkl* within the range $3° \leqslant 2\theta \leqslant 125°$, were recorded by the θ—2θ scan technique, with a 2θ velocity of 1° min^{-1}, and an asymmetric scan range from $(2\theta - 0{\cdot}75)°$ to $(2\theta + 0{\cdot}75 + \Delta)°$ (where Δ is the angular separation between the α_1 and α_2 components of the reflection concerned). Backgrounds were recorded for 20 s at the scan range limits, and were assumed to be linear

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[6] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1967, **22**, 457.

between these two points. Intensities of three reflections, distributed nearly orthogonally in reciprocal space and at a 2θ value of *ca.* 50—60°, were monitored after each 40 measurements. None showed a significant intensity variation during data collection. Graphite-crystal monochromated Cu-K_α radiation was used throughout.

Reflection data were reduced to values of $|F_o|$,† equivalent forms were averaged, and each reflection was assigned an individual estimated standard deviation, $\sigma(F_o)$: $\sigma(F_o) = [LP^{-2} \times \Delta I^2 + (\rho F_o{}^2)^2]^{\frac{1}{2}}/2F_o$, where $\Delta I = [CT + (t_p/t_b)^2(B_1 + B_2)]^{\frac{1}{2}}$, LP is the Lorentz-polarization correction, CT is the integrated reflection intensity, t_p is the reflection scan time, t_b is the total background counting time (=40 s), B_1 and B_2 are the individual background counts, and ρ [$= (0{\cdot}001)^{\frac{1}{2}}$] is the instrumental 'uncertainty factor.'[7,8] Reflections for which the individual background measurements differed significantly [*i.e.* if $(|B_1 - B_2|)/(B_1 + B_2)^{\frac{1}{2}} \geqslant 4{\cdot}0$] were discarded, as were those for which $I/\Delta I < 3{\cdot}0$ [$I = CT - (t_p/t_b)(B_1 + B_2)$]. The resultant data set comprised 2776 unique reflections. The statistical R for this terminal data set, defined as $R_s = \Sigma\sigma_s(F_o)/\Sigma|F_o|$ [$\sigma_s(F_o) = LP^{-1} \times \Delta I/2F_o$], is 0·030.

Solution and Refinement of the Structure.—The co-ordinates of all non-hydrogen atoms were readily obtained from conventional Patterson and Fourier synthesis. Initial full-matrix least-squares refinement, with individual isotropic temperature factors for all atoms, rigid-body positional parameters for the six phenyl rings, and individual positional parameters for the remaining atoms, rapidly converged to R 0·088 and R' [$= \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{\frac{1}{2}}$] 0·090 [with equal (unit) weights]. Atomic scattering factors were taken from ref. 9, those for iron and phosphorus being corrected for both real and imaginary anomalous scattering contributions.[10,11]

Data were subsequently corrected for absorption effects, by use of a 10 × 4 × 4 grid in the *a*, *b*, and *c** directions. Further refinement of individual atom co-ordinates, isotropic thermal parameters, and overall scale factor, by use of a block-diagonal least-squares approximation, with individual weights [$w = 1/\sigma^2(F_o)$] converged with R 0·086 and R' 0·100. Introduction of anisotropic thermal parameters [$T = \exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)$] for all atoms further reduced these values to R 0·068 and R' 0·079.

At this stage of refinement, a difference-Fourier synthesis showed phenyl hydrogen atoms in stereochemically reasonable positions. Accurate map co-ordinates could not be obtained, and consequently, they were included as fixed contributions to F_c on the basis of idealized co-ordinates (assuming C–H 1·087 Å) with fixed isotropic temperature factors ($B_H = B_C + 1{\cdot}0$ Å^2). These values were recalculated after each adjustment of the non-hydrogen atom parameters. With the phenyl hydrogen atom contributions included, refinement converged (with all parameter shifts $< 0{\cdot}1\sigma$) with R 0·050 and R' 0·056.

The estimated standard deviation of an observation of unit weight [defined as $\Sigma w(F_o - F_c)^2/(m - n)$, where m = number of observations, n (= 424) is the number of parameters varied], is 2·02, *cf.* 1·00 for ideal weighting. Comparison of the observed and calculated structure factor amplitudes, showed no evidence of serious extinction effects, and no correction was thought necessary. Similarly, no serious dependence of $w(F_o - F_c)^2$ on either F_o or $\sin\theta/\lambda$, was apparent. The final scattering model does not include vinyl hydrogen atom contributions. These were apparent on a final difference-Fourier map as very diffuse peaks with maxima of *ca.* 0·5 eÅ^{-3}, but at no stage were included in the refinement. No other positive maxima of density $> 0{\cdot}3$ eÅ^{-3} were observed. Terminal atom co-ordinates and thermal parameters, together with their estimated standard deviations (obtained from inversion of the block-diagonal matrices), are listed in Table 1.

Calculations were performed on a CDC 3600 computer at the C.S.I.R.O. Division of Computing Research, Canberra, and an IBM 360/50 computer at The Australian National University. Least-squares refinements were carried out with modified versions of Prewitt's program SFLS-5,[10] and absorption corrections with a modified version of ACACA.[12] Figures 1 and 2 were produced by ORTEP.[13] Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20770 (2 pp., 1 microfiche).‡

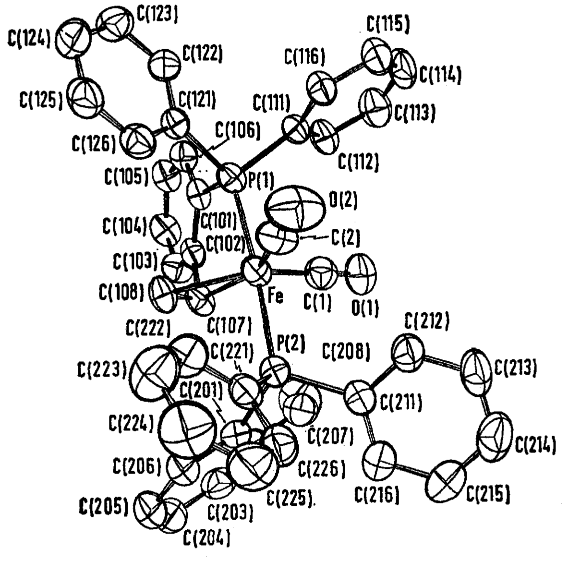

FIGURE 1 The overall stereochemistry of the molecule, together with the atom numbering scheme

RESULTS AND DISCUSSION

The crystal structure, as defined by the unit-cell parameters, symmetry operations, and atom co-ordinates of Table 1, consists of well separated monomeric units. The molecule has neither crystallographic nor virtual symmetry higher than C_1. The overall stereochemistry

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† The Lorentz-polarization correction takes the form $LP = (\cos^2 2\theta + \cos^2 2\theta_m)/[\sin 2\theta\ (1 + \cos^2 2\theta_m)]$ where θ and θ_m (= 13·25°) are the Bragg angles for the reflection and the monochromator respectively.

‡ See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-size copies.)

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TABLE 1

Atomic positional and thermal parameters

(*a*) Refined positional and anisotropic thermal parameters

Atom	*x*/*a*	*y*/*b*	*z*/*c*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0·20174(6)	0·25979(5)	0·10215(4)	0·00341(5)	0·00228(3)	0·00132(2)	−0·00002(3)	−0·00013(2)	0·00000(2)
P(1)	0·21733(10)	0·34624(8)	0·04224(6)	0·00316(8)	0·00223(5)	0·00128(3)	0·00022(5)	−0·00010(4)	−0·00007(3)
P(2)	0·19904(10)	0·16906(8)	0·16252(6)	0·00334(9)	0·00265(6)	0·00145(3)	−0·00042(5)	−0·00013(4)	0·00018(3)
O(1)	0·0200(2)	0·2914(2)	0·1012(2)	0·0037(2)	0·0044(2)	0·0028(1)	0·0000(2)	0·0000(1)	−0·0002(1)
O(2)	0·2183(3)	0·1564(2)	0·0140(2)	0·0114(4)	0·0037(2)	0·0020(1)	−0·0001(2)	0·0011(2)	−0·0009(1)
C(1)	0·0920(4)	0·2781(3)	0·1017(2)	0·0046(4)	0·0029(2)	0·0017(1)	−0·0002(2)	0·0002(2)	−0·0001(1)
C(2)	0·2139(4)	0·1965(3)	0·0506(2)	0·0058(4)	0·0030(2)	0·0015(1)	0·0001(2)	0·0002(2)	0·0001(1)
C(101)	0·2268(3)	0·4295(3)	0·0830(2)	0·0026(3)	0·0022(2)	0·0016(1)	0·0001(2)	−0·0002(2)	−0·0003(1)
C(102)	0·2296(3)	0·4143(3)	0·1396(2)	0·0028(3)	0·0031(2)	0·0013(1)	0·0001(2)	0·0000(1)	−0·0004(1)
C(103)	0·2266(4)	0·4727(3)	0·1754(2)	0·0057(4)	0·0028(2)	0·0017(1)	0·0000(2)	0·0002(2)	−0·0003(1)
C(104)	0·2262(4)	0·5432(3)	0·1563(2)	0·0053(4)	0·0026(2)	0·0020(1)	0·0005(2)	−0·0001(2)	−0·0007(1)
C(105)	0·2305(4)	0·5573(3)	0·1009(2)	0·0044(4)	0·0022(2)	0·0022(1)	0·0005(2)	−0·0002(2)	−0·0001(1)
C(106)	0·2285(4)	0·5005(3)	0·0641(2)	0·0035(3)	0·0022(2)	0·0019(1)	0·0038(2)	0·0001(2)	0·0001(1)
C(107)	0·2424(4)	0·3379(3)	0·1618(2)	0·0046(4)	0·0017(2)	0·0017(1)	−0·0004(2)	−0·0008(2)	−0·0002(1)
C(108)	0·3160(3)	0·2982(3)	0·1475(2)	0·0032(3)	0·0021(2)	0·0017(1)	−0·0001(2)	−0·0003(2)	−0·0006(1)
C(111)	0·1250(3)	0·3572(3)	−0·0111(2)	0·0028(3)	0·0025(2)	0·0013(1)	0·0003(2)	−0·0001(2)	0·0001(1)
C(112)	0·0549(4)	0·3985(3)	−0·0010(2)	0·0034(3)	0·0032(2)	0·0020(1)	0·0005(2)	−0·0005(2)	−0·0001(1)
C(113)	−0·0192(4)	0·3970(3)	−0·0386(3)	0·0040(4)	0·0039(3)	0·0026(2)	0·0009(3)	−0·0004(2)	0·0001(2)
C(114)	−0·0233(4)	0·3550(3)	−0·0858(3)	0·0034(4)	0·0041(3)	0·0024(2)	−0·0001(3)	−0·0010(2)	0·0003(2)
C(115)	0·0460(4)	0·3151(3)	−0·0962(2)	0·0040(4)	0·0037(3)	0·0018(1)	−0·0005(2)	−0·0004(2)	0·0000(2)
C(116)	0·1204(4)	0·3160(3)	−0·0586(2)	0·0031(3)	0·0030(2)	0·0015(1)	0·0000(2)	−0·0001(2)	−0·0001(1)
C(121)	0·3081(3)	0·3498(3)	0·0028(2)	0·0031(3)	0·0026(2)	0·0012(1)	−0·0005(2)	0·0000(1)	−0·0002(1)
C(122)	0·3129(4)	0·4046(3)	−0·0357(2)	0·0037(3)	0·0027(2)	0·0015(1)	−0·0001(2)	0·0002(2)	0·0003(1)
C(123)	0·3862(4)	0·4120(3)	−0·0611(2)	0·0050(4)	0·0032(2)	0·0018(1)	−0·0005(2)	0·0006(2)	0·0003(2)
C(124)	0·4541(4)	0·3646(3)	−0·0490(2)	0·0039(4)	0·0047(3)	0·0019(1)	−0·0006(3)	0·0007(2)	−0·0003(2)
C(125)	0·4480(4)	0·3081(3)	−0·0126(2)	0·0034(4)	0·0044(3)	0·0018(1)	0·0009(2)	0·0001(2)	0·0000(2)
C(126)	0·3756(4)	0·3003(3)	0·0138(2)	0·0037(3)	0·0030(2)	0·0015(1)	0·0004(2)	0·0001(2)	0·0001(1)
C(201)	0·2278(4)	0·1917(3)	0·2362(2)	0·0036(3)	0·0031(2)	0·0013(1)	−0·0005(2)	0·0002(2)	0·0005(1)
C(202)	0·1768(4)	0·2370(3)	0·2650(2)	0·0044(4)	0·0036(3)	0·0015(1)	−0·0009(2)	0·0006(2)	0·0003(1)
C(203)	0·2079(4)	0·2561(3)	0·3199(2)	0·0058(4)	0·0039(3)	0·0016(1)	−0·0008(3)	0·0008(2)	0·0001(2)
C(204)	0·2865(4)	0·2328(4)	0·3452(2)	0·0055(4)	0·0054(3)	0·0013(1)	−0·0017(3)	−0·0001(2)	−0·0001(2)
C(205)	0·3370(4)	0·1898(4)	0·3165(2)	0·0046(4)	0·0053(3)	0·0017(1)	−0·0010(3)	−0·0004(2)	0·0003(2)
C(206)	0·3080(4)	0·1693(3)	0·2626(2)	0·0039(4)	0·0042(3)	0·0016(1)	−0·0005(2)	−0·0001(2)	0·0003(1)
C(207)	0·0923(4)	0·2651(4)	0·2383(3)	0·0040(4)	0·0050(3)	0·0021(2)	0·0009(2)	0·0008(2)	0·0005(2)
C(208)	0·0574(5)	0·3266(4)	0·2538(3)	0·0075(5)	0·0065(4)	0·0035(2)	0·0016(4)	0·0012(3)	−0·0003(2)
C(211)	0·0999(4)	0·1169(3)	0·1594(2)	0·0038(4)	0·0031(2)	0·0017(1)	−0·0005(2)	−0·0003(2)	0·0003(1)
C(212)	0·0536(4)	0·1028(3)	0·1083(2)	0·0037(4)	0·0022(2)	0·0022(1)	−0·0002(2)	−0·0003(2)	0·0003(1)
C(213)	−0·0188(4)	0·0585(3)	0·1034(3)	0·0034(4)	0·0029(2)	0·0030(2)	−0·0001(2)	−0·0010(2)	0·0001(1)
C(214)	−0·0450(4)	0·0285(4)	0·1486(3)	0·0036(4)	0·0038(3)	0·0041(2)	−0·0005(3)	−0·0002(2)	0·0007(2)
C(215)	−0·0013(5)	0·0428(4)	0·2007(3)	0·0071(5)	0·0065(4)	0·0030(2)	−0·0031(4)	0·0004(3)	0·0013(2)
C(216)	0·0716(4)	0·0872(4)	0·2056(3)	0·0058(4)	0·0061(4)	0·0022(1)	−0·0028(3)	−0·0002(2)	0·0007(2)
C(221)	0·2753(3)	0·0960(3)	0·1538(2)	0·0034(3)	0·0024(2)	0·0014(1)	0·0000(2)	−0·0003(2)	0·0001(1)
C(222)	0·3512(4)	0·1118(3)	0·1336(2)	0·0044(4)	0·0026(2)	0·0024(2)	0·0006(2)	0·0006(2)	0·0002(2)
C(223)	0·4110(4)	0·0579(3)	0·1290(3)	0·0052(4)	0·0036(3)	0·0034(2)	0·0007(3)	0·0014(2)	0·0001(2)
C(224)	0·3943(4)	−0·0127(3)	0·1422(3)	0·0070(5)	0·0025(2)	0·0034(2)	0·0010(3)	0·0002(2)	0·0000(2)
C(225)	0·3191(4)	−0·0293(3)	0·1609(3)	0·0072(5)	0·0024(2)	0·0027(2)	−0·0004(3)	−0·0003(2)	0·0003(2)
C(226)	0·2593(4)	0·0246(3)	0·1673(2)	0·0043(4)	0·0029(2)	0·0021(1)	−0·0006(2)	−0·0006(2)	0·0003(2)

(*b*) Calculated hydrogen atom positional and thermal parameters

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*/Å^2	Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*/Å^2
H(103)	0·226	0·462	0·219	5·5	H(203)	0·168	0·290	0·342	5·9
H(104)	0·226	0·588	0·185	5·6	H(204)	0·309	0·249	0·387	6·3
H(105)	0·231	0·613	0·086	5·2	H(205)	0·399	0·171	0·336	6·4
H(106)	0·229	0·511	0·021	4·7	H(206)	0·347	0·135	0·240	5·5
H(112)	0·058	0·431	0·036	5·3	H(212)	0·075	0·126	0·072	5·1
H(113)	−0·074	0·429	−0·031	6·2	H(213)	−0·054	0·047	0·063	6·0
H(114)	−0·081	0·354	−0·115	6·1	H(214)	−0·101	−0·006	0·144	7·2
H(115)	0·042	0·283	−0·133	5·5	H(215)	−0·023	0·019	0·237	8·7
H(116)	0·175	0·284	−0·067	4·6	H(216)	0·107	0·099	0·246	7·5
H(122)	0·260	0·442	−0·045	4·6	H(222)	0·364	0·167	0·123	5·5
H(123)	0·390	0·456	−0·090	5·5	H(223)	0·471	0·071	0·114	6·9
H(124)	0·511	0·370	−0·069	5·9	H(224)	0·441	−0·055	0·138	7·2
H(125)	0·501	0·270	−0·004	5·6	H(225)	0·306	−0·085	0·172	6·7
H(126)	0·371	0·257	0·043	4·8	H(226)	0·199	0·011	0·182	5·5

of the molecule, together with the atom numbering scheme, is shown in Figure 1, while a stereoscopic view of the molecule is given in Figure 2. In both Figures, the thermal ellipsoids have been drawn to include 50% of the probability distribution, and for clarity, hydrogen atoms have been omitted. Principal interatomic distances and inter-bond angles, together with their estimated standard deviations, are listed in Table 2 and Table 3 respectively. The results of weighted least-squares planes calculations are collected in Table 4.[14]

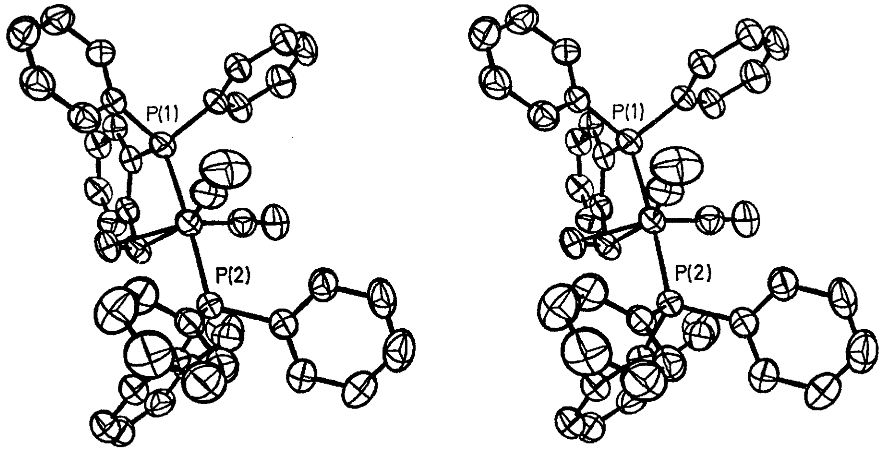

FIGURE 2 A stereoscopic view of the molecule

TABLE 2

Bond lengths (Å) with estimated standard deviations in parentheses

Fe–P(1)	2·205(2)	Fe–P(2)	2·239(2)
Fe–C(1)	1·763(6)	Fe–C(2)	1·751(6)
Fe–C(107)	2·092(5)	Fe–C(108)	2·108(5)
C(1)–O(1)	1·160(7)	C(2)–O(2)	1·172(7)
P(1)–C(101)	1·828(5)	P(1)–C(111)	1·831(5)
P(1)–C(121)	1·833(5)	P(2)–C(201)	1·848(6)
P(2)–C(211)	1·829(6)	P(2)–C(221)	1·839(6)
C(101)–C(102)	1·411(7)	C(102)–C(103)	1·394(8)
C(103)–C(104)	1·383(8)	C(104)–C(105)	1·393(8)
C(105)–C(106)	1·378(8)	C(101)–C(106)	1·393(7)
C(102)–C(107)	1·515(8)	C(107)–C(108)	1·455(8)
C(111)–C(112)	1·392(7)	C(112)–C(113)	1·387(9)
C(113)–C(114)	1·385(9)	C(114)–C(115)	1·371(9)
C(115)–C(116)	1·389(8)	C(111)–C(116)	1·385(7)
C(121)–C(122)	1·393(8)	C(122)–C(123)	1·392(8)
C(123)–C(124)	1·384(9)	C(124)–C(125)	1·385(9)
C(125)–C(126)	1·394(8)	C(121)–C(126)	1·402(8)
C(201)–C(202)	1·414(8)	C(202)–C(203)	1·412(8)
C(203)–C(204)	1·378(9)	C(204)–C(205)	1·381(9)
C(205)–C(206)	1·391(8)	C(201)–C(206)	1·403(8)
C(202)–C(207)	1·496(9)	C(207)–C(208)	1·339(10)
C(211)–C(212)	1·386(8)	C(212)–C(213)	1·397(8)
C(213)–C(214)	1·351(10)	C(214)–C(215)	1·393(10)
C(215)–C(216)	1·403(10)	C(211)–C(216)	1·385(9)
C(221)–C(222)	1·386(8)	C(222)–C(223)	1·386(9)
C(223)–C(224)	1·378(9)	C(224)–C(225)	1·364(10)
C(225)–C(226)	1·395(10)	C(221)–C(226)	1·391(8)

As predicted from ^{1}H n.m.r. and i.r. data, the molecule is approximately trigonal bipyramidal, with the two phosphorus atoms occupying axial sites. The two carbonyl groups, and a π-bonded vinyl substituent of one (2-vinylphenyl)diphenylphosphine ligand occupy the equatorial sites. The differing character of the two sp groups (one chelated and one unidentate *P*-bonded) is clearly shown by the ^{1}H n.m.r. spectra which show

TABLE 3

Bond angles (°) with estimated standard deviations in parentheses

P(1)–Fe–P(2)	174·48(7)	P(1)–Fe–C(1)	93·1(2)
P(1)–Fe–C(2)	88·3(2)	P(1)–Fe–C(107)	85·1(2)
P(1)–Fe–C(108)	86·8(2)	P(2)–Fe–C(1)	92·4(2)
P(2)–Fe–C(2)	89·4(2)	P(2)–Fe–C(107)	94·9(2)
P(2)–Fe–C(108)	89·7(2)	C(1)–Fe–C(2)	109·1(3)
C(1)–Fe–C(107)	94·6(2)	C(1)–Fe–C(108)	135·0(2)
C(2)–Fe–C(107)	155·7(2)	C(2)–Fe–C(108)	115·9(3)
C(107)–Fe–C(108)	40·5(2)	Fe–C(1)–O(1)	178·8(5)
Fe–C(2)–O(2)	175·9(6)	Fe–C(107)–C(108)	70·3(3)
Fe–C(108)–C(107)	69·1(3)	Fe–C(107)–C(102)	112·2(4)
Fe–P(1)–C(101)	104·7(2)	Fe–P(1)–C(111)	113·9(2)
Fe–P(1)–C(121)	122·8(2)	C(101)–P(1)–C(111)	107·1(2)
C(101)–P(1)–C(121)	104·2(2)	C(111)–P(1)–C(121)	102·8(2)
Fe–P(2)–C(201)	116·8(2)	Fe–P(2)–C(211)	117·3(2)
Fe–P(2)–C(221)	113·7(2)	C(201)–P(2)–C(211)	104·8(3)
C(201)–P(2)–C(221)	101·6(2)	C(211)–P(2)–C(221)	100·2(3)
P(1)–C(101)–C(102)	111·1(4)	P(1)–C(101)–C(106)	127·9(4)
C(102)–C(101)–C(106)	120·9(5)	C(101)–C(102)–C(103)	117·1(5)
C(102)–C(103)–C(104)	121·0(5)	C(103)–C(104)–C(105)	120·5(5)
C(104)–C(105)–C(106)	119·6(5)	C(101)–C(106)–C(105)	119·9(5)
C(101)–C(102)–C(107)	121·5(5)	C(103)–C(102)–C(107)	120·6(5)
C(102)–C(107)–C(108)	117·1(5)	P(1)–C(111)–C(112)	120·5(4)
P(1)–C(111)–C(116)	119·1(4)	C(112)–C(111)–C(116)	119·8(5)
C(111)–C(112)–C(113)	119·3(5)	C(112)–C(113)–C(114)	120·4(6)
C(113)–C(114)–C(115)	120·5(6)	C(114)–C(115)–C(116)	119·5(6)
C(111)–C(116)–C(115)	120·5(5)	P(1)–C(121)–C(122)	120·1(4)
P(1)–C(121)–C(126)	120·2(4)	C(122)–C(121)–C(126)	119·6(5)
C(121)–C(122)–C(123)	120·0(5)	C(122)–C(123)–C(124)	120·5(5)
C(123)–C(124)–C(125)	119·8(6)	C(124)–C(125)–C(126)	120·6(5)
C(121)–C(126)–C(125)	119·5(5)	P(2)–C(201)–C(202)	122·7(4)
P(2)–C(201)–C(206)	118·1(4)	C(202)–C(201)–C(206)	118·8(5)
C(201)–C(202)–C(203)	118·3(5)	C(202)–C(203)–C(204)	121·8(6)
C(203)–C(204)–C(205)	119·7(6)	C(204)–C(205)–C(206)	120·1(6)
C(201)–C(206)–C(205)	121·2(6)	C(201)–C(202)–C(207)	121·3(5)
C(203)–C(202)–C(207)	120·3(5)	C(202)–C(207)–C(208)	123·1(6)
P(2)–C(211)–C(212)	118·7(4)	P(2)–C(211)–C(216)	122·9(5)
C(212)–C(211)–C(216)	118·3(6)	C(211)–C(212)–C(213)	120·9(5)
C(212)–C(213)–C(214)	120·4(6)	C(213)–C(214)–C(215)	120·4(6)
C(214)–C(215)–C(216)	119·1(6)	C(211)–C(216)–C(215)	120·9(6)
P(2)–C(221)–C(222)	119·8(4)	P(2)–C(221)–C(226)	121·7(4)
C(222)–C(221)–C(226)	118·5(5)	C(221)–C(222)–C(223)	120·5(6)
C(222)–C(223)–C(224)	120·5(6)	C(223)–C(224)–C(225)	119·6(7)
C(224)–C(225)–C(226)	120·6(6)	C(221)–C(226)–C(225)	120·2(5)

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[14] The method of weighting least-squares planes is outlined in Ref. 9, vol. II, p. 93.

signals attributable to both co-ordinated and un-co-ordinated vinyl groups in a 1 : 1 ratio.

The angles at the central iron atom indicate some deviation from strictly trigonal symmetry. In particular, within the equatorial plane, the angles C(1)–Fe–MPV, 114·9°, and C(2)–Fe–MPV, 135·8°, are significantly different from the expected value of *ca.* 125° [MPV is the mid-point of the C(107)–C(108) bond]. This distortion is presumably strain-induced, and associated with fitting the chelated sp ligand around the metal atom.

TABLE 4

Some important least-squares planes [a] [atom deviations (Å) are listed in square brackets]

Plane (1): Fe, C(1), C(2)
$-0·1493X - 0·7436Y + 0·6517Z + 2·3765 = 0$
[P(1) −2·201, P(2) 2·237, O(1) −0·022, O(2) −0·058, C(107) −0·196, C(108) −0·056]

Plane (2): Fe, C(107), C(108)
$-0·1963X - 0·6639Y + 0·7216Z + 1·9541 = 0$
[P(1) −2·197, P(2) 2·217, O(1) 0·158, O(2) −0·385, C(1) 0·108, C(2) −0·198]

(3): Ph rings bonded to P(1)
C(101)—(106): $0·9898X - 0·0027Y + 0·1426Z - 3·5579 = 0$
C(111)—(116): $-0·4064X - 0·7741Y + 0·4854Z + 6·0579 = 0$
C(121)—(126): $0·3124X + 0·5931Y + 0·7421Z - 5·3804 = 0$

n = 0,1,2	C(101)—(106)	C(111)—(116)	C(121)—(126)
C(1n1)	−0·024	0·004	0·016
C(1n2)	0·032	−0·004	−0·014
C(1n3)	−0·011	−0·001	−0·003
C(1n4)	−0·024	0·006	0·019
C(1n5)	0·031	−0·004	−0·012
C(1n6)	−0·004	−0·001	−0·006
P(1)	−0·175	0·270	0·200
C(107)	0·239		
C(108)	1·388		

(4): Ph rings bonded to P(2)
C(201)—(206): $-0·4770X - 0·8129Y + 0·3341Z + 2·3128 = 0$
C(211)—(216): $-0·5907X + 0·8028Y + 0·0884Z - 1·4625 = 0$
C(221)—(226): $0·3093X + 0·1652Y + 0·9365Z - 4·9693 = 0$

n = 0,1,2	C(201)—(206)	C(211)—(216)	C(221)—(226)
C(2n1)	0·008	−0·008	0·006
C(2n2)	−0·009	0·004	−0·014
C(2n3)	0·003	0·003	0·012
C(2n4)	0·006	−0·011	0·002
C(2n5)	−0·006	0·007	−0·009
C(2n6)	−0·002	0·005	0·003
P(2)	−0·149	−0·146	0·046
C(207)	−0·054		
C(208)	−0·565		

[a] The plane equations $lX + mY + nZ - D = 0$ refer to orthogonal axes where

$X = 15·7715x + 0·0y - 3·3073z$
$Y = 0·0x + 18·4683y + 0·0z$
$Z = 0·0x + 0·0y + 24·2743z$

Consistent with its formulation as a π-bonded group, the vinyl substituent of the chelated sp ligand C(107)–C(108) shows the expected lengthening consequent upon co-ordination to the iron atom. Thus, the observed bond length [1·455(8) Å] is intermediate between the accepted values of 1·337(6),[15a] and 1·541(3) Å,[15b] for carbon–carbon double- and single-bonds respectively. Similar bond-lengthening has been observed for the acrylonitrile complex [$Fe(CO)_4(CH_2⁚CHCN)$] [16] where the C⁚C distance is 1·40 Å. The corresponding distances observed for the fumaric acid derivatives [(−)-$Fe(CO)_4(CHCO_2H)_2$] [17] and [(*rac*)-$Fe(CO)_4(CHCO_2H)_2$],[18] are 1·40(5) and 1·42(4) Å respectively. Although not particularly accurate, the results of a recent electron-diffraction study suggest that the olefinic distance in the ethylene complex [$Fe(CO)_4(CH_2⁚CH_2)$] is 1·46(6) Å.[19] In contrast, the vinyl substituent of the unidentate *P*-bonded sp ligand in the present complex [C(207)–C(208) **1·339(10)** Å] is as expected for a 'free' vinyl group. Moreover, the distances Fe–C(207) and Fe–C(208) (3·96 and 4·77 Å), indicate that there are no interactions between the iron atom and this vinyl group.

The metal–olefin bonding is symmetrical, with Fe–C(vinyl) distances [Fe–C(107) 2·092(5), Fe–C(108) 2·108(5) Å] equal and, generally, in good agreement with those values reported for other mono-olefin iron(0) complexes.[16-18] The olefin is rotated only slightly from the equatorial plane [the dihedral angle between the weighted planes defined by Fe, C(1), C(2) and Fe, C(107), C(108) is 6·65°] despite there being fairly substantial angular deformations within the chelate ring system Fe–P(1)–C(101)–C(102)–C(107)⁚C(108). In particular, the angles Fe–P(1)–C(101) [104·7(2)°], P(1)–C(101)–C(102) [111·1(4)°], and P(1)–C(101)–C(106) [127·9(4)°], differ markedly from their expected values of *ca.* 115, 120, and 120°. Along with these angular deformations there is a small, but significant, degree of strain-induced aplanarity in the C(101)—(106) ring system, and in addition, a marked deviation of the vinyl α-carbon atom [C(107), Δ 0·24 Å] from the weighted C(101)—(106) least-squares plane.

The individual Fe–C(carbonyl) distances [1·763(6) and 1·751(6) Å] are equal within experimental error, mean 1·757(4) Å. This may be compared with the corresponding values for the parent carbonyl $Fe(CO)_5$ [1·833(4) Å] [20, 21] and for the monophosphine derivatives $Fe(CO)_4(PHPh_2)$ [1·790(5) Å] [22] and [$Fe(CO)_4(PMe_2)$]$_2$ [1·79(2)].[23] The smooth decrease in Fe–C(carbonyl) distance on passing from the parent pentacarbonyl through the mono- to the bis-phosphine derivative is clearly a consequence of the differing characters of carbonyl and phosphine ligands. In particular, the strong-donor–weak-acceptor properties of the phosphine ligands serve to force a much higher π-character on the remaining metal–

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carbonyl bonds. The concomitant decrease in C–O bond-order is reflected quite clearly in the steady decrease in ν(CO) frequencies through the series $Fe(CO)_5$,[24] $Fe(CO)_3(sp)$,[5] and $Fe(CO)_2(sp)_2$.[5] As expected, the C–O(carbonyl) distances in the present complex [1·160(7) and 1·172(7)Å] are only slightly longer than those found in free carbon monoxide, while the Fe–C–O angles show the usual slight deviation from linearity. Reasons for this deviation have been detailed previously.[25]

The near-equivalence of equatorial metal–carbonyl distances in the present complex and in $[Fe(CO)_4(CH_2{:}CHCN)]$ [16] appears to have no obvious rationale, except perhaps, as a consequence of the unusually long axial metal–carbonyl bond (1·99 Å) observed in the latter complex. It seems likely that this, in turn, must be a consequence of crystal packing rather than of electronic origin.

The Fe–P(2) distance [2·239(2) Å] is in excellent agreement with that [2·237(2) Å] found for $[Fe(CO)_4(PHPh_2)]$.[22] In turn, these values are only slightly shorter than those of 2·25 and 2·26 Å found for $[Fe_3(CO)_{11}(PPh_3)]$,[26] and $[Fe(CO)_4(PMe_2)]_2$.[23] In contrast, the corresponding distance in the chelated sp ligand in the present complex [Fe–P(1) 2·205(2) Å, Δ/σ 19] is significantly shorter, the contraction reflecting the marked chelating ability of sp.

The geometry of co-ordinated triphenylphosphine ligands is well known, and has been discussed in detail in many other papers. Apart from the angular anomalies resulting from chelation of the sp ligand, there are no obvious abnormalities in the geometries of the two co-ordinated phosphine ligands. Thus, the Fe–P–C angles, apart from Fe–P(1)–C(101), are significantly larger than the normal tetrahedral angle, while the six C–P–C are all significantly less than the tetrahedral angle. The mean phenyl ring C–C distance is 1·389 Å, mean C–C–C angle 120·0°.

The distances C(102)–C(107) [1·515(8) Å] and C(202)–C(207) [1·496(9) Å], and the angles C(101–C(102)–C(107) [121·5(5)°], C(102)–C(107)–C(108) [117·1(5)°], C(201)–C(202)–C(207) [121·3(5)°], and C(202)–C(207)–C(208) [123·1(6)°], are all as expected.

There are no intermolecular contacts shorter than the sums of the appropriate van der Waals radii.

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