al., 1980; Bau *et al.*, 1977; Iball *et al.*, 1975). The bond distances and angles within the *N*,*N*-dimethylethylenediamine ligand are normal (Table 2). The torsion angles have been calculated and deposited.

In the structure of [PtCl₂(en)] the Pt(en) chelate rings are puckered and the distance between adjacent Pt atoms is 3·38 Å (Iball *et al.*, 1975). In the present structure, the Pt atoms cannot be so close because of the presence of two methyl groups, one on each side of the Pt coordination plane. The shortest distance is 5·639 Å. The packing of the molecules in the crystal is shown in Fig. 2. It consists of layers of molecules parallel to the *ac* plane and centered at $y = 0.3$ and 0.8. The crystal is probably stabilized by intermolecular hydrogen bonding between the $-NH_2$ group and Cl(2). The $N(1)\cdots Cl(2)$ distances are 3·37 (1) and 3·58 (1) Å and the angles are acceptable (Table 2).

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Structure of the Phosphorin Derivative [Fe(η⁵-C₅H₅)(CO)₂{(CH₃)PC₅H₂(C₆H₅)₃}]

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Abstract. Dicarbonyl(η-cyclopentadienyl)(1-methyl-2,4,6-triphenylphosphorin)iron, $C_{31}H_{25}FeO_2P$, $M_r = 516.36$, monoclinic, $P2_1/a$, $a = 9.482$ (3), $b = 14.051$ (4), $c = 18.941$ (4) Å, $\beta = 94.80$ (2)°, $V = 2514.7$ Å³, $Z = 4$, $D_x = 1.364$, D_m (by flotation) = 1·39 Mg m⁻³, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 6.35$ mm⁻¹, $F(000) = 1072$, $T = 298$ K. Final $wR = 0.050$ ($R = 0.071$) for 994 observed independent reflections. The structure consists of discrete molecules; the phosphorin ligand is bound to the iron *via* the P atom. The five C atoms of the phosphorin ring do not deviate noticeably from planarity; the C–C distances are equal within 1σ [mean 1·40 (2) Å]. The 'chair angle' between the carbon plane C(1)–C(5) and the plane C(1), P, C(5) is 23·2°. There exists an obvious relationship with the 'open ferrocenes'.

Introduction. The complex chemistry of phosphorin ligands has only recently been studied in detail (Dave, Berger, Bilger, Kaletsch, Pebler, Knecht & Dimroth, 1985; Lehmkuhl, Elsässer, Benn, Gabor, Rufinska, Goddard & Krüger, 1985). Interest in this chemistry stems from the close relationship with the ferrocenes (I) and the so-called 'open ferrocenes' (II) with an open five-membered pentadienyl ligand (Ernst, 1985). Phosphorin ligands can coordinate in several ways, as shown in the scheme. The phosphorin sandwich (III) has a *gauche*-eclipsed conformation with both ligands η⁵-bonded (Baum & Massa, 1985) and the same type of bonding was found in chloro(diethyl ether)(1-isopropyl-2,4,6-triphenylphosphorin)magnesium, [MgCl(CH₃)₂CHPC₅H₂(C₆H₅)₃{O(C₂H₅)₂}]₂, (Krüger, 1985, unpublished). The η³-allyl-type bonding in (V) has been deduced from NMR experiments (Lehmkuhl, Elsässer, Benn, Gabor, Rufinska, Goddard & Krüger, 1985) and an X-ray structure determination established bonding of the P atom to the central Ni atom in (IV) (Lehmkuhl, Elsässer, Benn, Gabor, Rufinska, Goddard & Krüger, 1985). To elucidate more of the complex chemistry of phosphorin ligands a single X-ray structure determination has been performed of the title compound (VI). (VI) can be synthesized by reacting cpFe(CO)₂I with (1-methyl-2,4,6-triphenylphosphorin)lithium (Dave, Berger, Bilger, Kaletsch, Pebler, Knecht & Dimroth, 1985).

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(I)   (II)   (III)   (IV)   (V)

a   b   c

(VI)
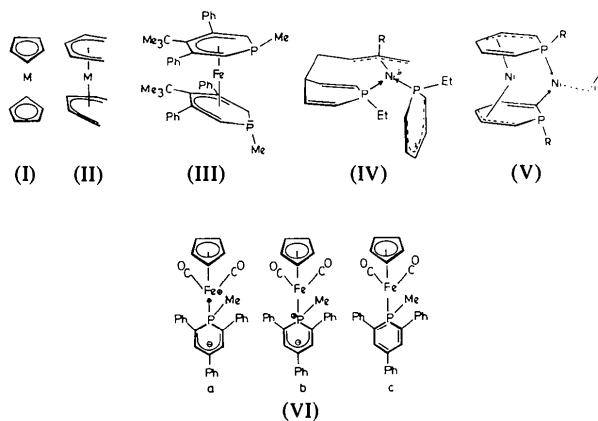
Experimental. Highly air-sensitive single crystals were obtained from benzene/hexane solutions (1:1). A needle-shaped crystal (0·12 × 0·24 × 0·6 mm) sealed in a glass capillary was used for investigation. Lattice parameters were derived from setting angles (6·5 ≤ $2\theta \leq 24\cdot2°$) of 40 machine-centred reflections (Siemens–Stoe AED2, monochromatic Mo $K\alpha$ radiation). Data collection (ω scans, $2\cdot5 \leq 2\theta \leq 60\cdot0°$, index range −13 to 13, −20 to 0 and 0 to 27) yielded 994 observed independent reflections with $I > 3\cdot0\sigma(I)$ (1021 unique reflections; 4385 unobserved; equivalent reflections merged, $R_{int} = 0\cdot059$; systematic absences 0k0 $k = 2n+1$, h0l $h = 2n+1$). Two standard reflections (005: I_{max} 1217, I_{min} 1142; 130: 314, 248) measured every 2 h, no significant fluctuations observed. Lorentz and polarization corrections as well as an empirical (ψ scans of four reflections with 5·2 < $2\theta < 18\cdot0°$, min. transmission 0·624, max. = 0·753) absorption correction applied.

The crystal system is monoclinic with space group $P2_1/a$ (C_{2h}^5). The position of the Fe atom was readily located by heavy-atom methods; the positions of the other non-hydrogen atoms were taken from Fourier maps. Final refinement by a cascaded block-matrix procedure based on F with anisotropic temperature factors for the Fe and P atoms and isotropic temperature factors for all the other non-hydrogen atoms. The H atoms were included 'riding' on the calculated positions (C—H distances fixed at 0·96 Å). $wR = 0\cdot050$ ($R = 0\cdot071$),* $S = 1\cdot32$, max. $\Delta/\sigma = -0\cdot01\,[z\,C(51)]$; largest features in final difference Fourier map: +0·25 and −0·20 e Å^{-3}. Weighting scheme $w = 1/\sigma(F)^2$; calculations performed on a Data General Eclipse computer, program packages: COSY85 (Stoe & Cie, 1985), STRUCSY84 (Stoe & Cie, 1984) and

SHELXTL (Sheldrick, 1983). Scattering factors including anomalous dispersion from *International Tables for X-ray Crystallography* (1974).

Table 1. *Atomic coordinates* (× 10⁴) *and equivalent isotropic temperature factors* (Fe, P) *and* U_{11} *values* (C,O)

	x	y	z	$U_{eq}(\text{Å}^2)^*$
Fe	222 (2)	448 (2)	1728 (1)	44 (2)
P(1)	−1829 (4)	−74 (3)	2175 (2)	41 (3)
C(1)	2379 (14)	1242 (10)	−1884 (8)	36 (4)
C(2)	2007 (12)	1991 (19)	−2329 (7)	31 (4)
C(3)	1614 (14)	1981 (10)	−3056 (8)	38 (5)
C(4)	1505 (14)	1084 (10)	−3402 (8)	50 (5)
C(5)	1722 (14)	168 (10)	−3118 (8)	40 (5)
C(6)	−3226 (12)	759 (9)	1871 (7)	56 (5)
C(11)	−107 (16)	1579 (12)	1986 (9)	70 (6)
O(11)	−258 (11)	2360 (7)	2160 (6)	81 (4)
C(12)	−651 (18)	591 (14)	917 (10)	81 (6)
O(12)	−1219 (11)	665 (8)	342 (7)	86 (4)
C(21)	2945 (16)	1391 (10)	−1140 (8)	45 (5)
C(22)	2131 (15)	1842 (10)	−649 (8)	51 (5)
C(23)	2702 (18)	2012 (12)	36 (10)	66 (6)
C(24)	4080 (16)	1683 (10)	240 (9)	51 (5)
C(25)	−4844 (16)	−1242 (10)	207 (8)	51 (5)
C(26)	4292 (15)	1087 (10)	−919 (8)	54 (5)
C(31)	1373 (15)	701 (10)	−3538 (8)	42 (5)
C(32)	2160 (16)	−1510 (11)	−3490 (9)	60 (6)
C(33)	1750 (19)	−2328 (13)	−3870 (9)	77 (6)
C(34)	619 (18)	−2282 (13)	−4359 (9)	81 (7)
C(35)	−192 (17)	−1488 (12)	−4457 (9)	71 (6)
C(36)	198 (14)	−680 (11)	−4059 (7)	53 (5)
C(41)	1347 (14)	2881 (10)	−3459 (8)	39 (5)
C(42)	2120 (14)	3038 (11)	−4055 (7)	46 (5)
C(43)	1931 (14)	3879 (10)	−4434 (8)	58 (5)
C(44)	1063 (14)	4565 (13)	−4218 (8)	56 (5)
C(45)	319 (14)	4412 (12)	−3635 (7)	52 (5)
C(46)	449 (15)	3577 (10)	−3218 (9)	47 (5)
C(51)	1228 (14)	−756 (11)	2250 (9)	56 (5)
C(52)	1850 (15)	94 (12)	2509 (9)	64 (6)
C(53)	2440 (13)	590 (11)	1933 (8)	49 (5)
C(54)	2186 (15)	54 (11)	1352 (9)	60 (6)
C(55)	1415 (15)	−768 (12)	1515 (9)	62 (6)

* $U_{eq} = \frac{1}{3}$ trace **U**, **U** signifying the diagonalized **U** matrix: $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \ldots)]$.
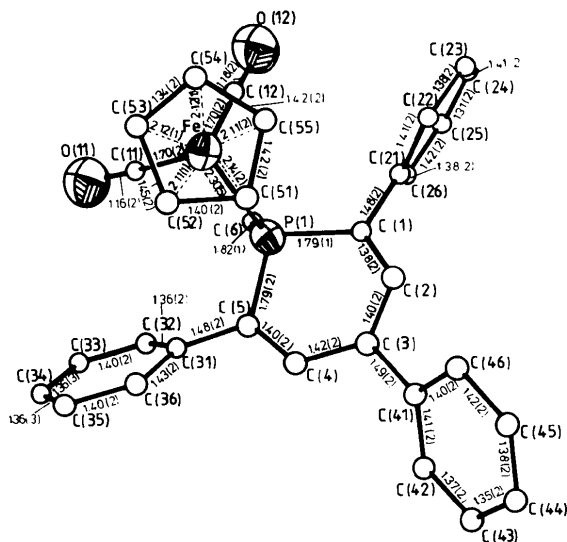

Fig. 1. The molecular structure and atomic numbering scheme of (VI). The thermal ellipsoids for Fe and P include 50% probability. The spheres for the O atoms correspond to isotropic U's, the C atoms are drawn as circles for clarity.

Discussion. Atomic coordinates are listed in Table 1, bond distances (in Å) in Fig. 1 and angles in Table 2; Fig. 1 shows a view of complex (VI) together with the numbering of the atoms. (VI) forms discrete molecules which, apart from the phenyl rings, approximately possess a mirror plane passing through C(41), C(3), P(1), C(51), Fe and the centre of the C(53)—C(54) bond. The iron atom is coordinated by a η^5-bonded cyclopentadienyl ligand, two carbonyl groups and the 1-methyl-2,4,6-triphenylphosphorin ring *via* the P atom. The coordination sphere around Fe is comparable to that of Mn in the isoelectronic η^5-C_5H_5-Mn(CO)$_3$ unit. The Fe—P distance [2·304 (5) Å] is in the range of a single bond; it is significantly longer than the Fe—P bond in (1-4-η-5-*exo*-benzylcyclopenta-1,3-diene)dicarbonyl(triphenylphosphine)iron(0) [mean 2·215 (2) Å] or dicarbonyl(η^5-cyclopentadienyl)(triphenylphosphine)iron(II) 1,1,2,3,3-pentacyanopropenide [2·240 (1) Å] (Sim, Woodhouse & Knox, 1979); it is thus indicated that there is no significant π back-bonding. Correspondingly the Fe—C(11) [1·70 (2)] and Fe—C(12) [1·70 (1) Å] distances do show considerable π back-bonding.

The five C atoms of the phosphorin ring do not deviate noticeably from planarity. The dihedral angle in the phosphorin ring ('chair angle') between the planes C(1), C(2), C(3), C(4), C(5) and C(1), P(1), C(5) is much smaller [23·2 (10)°] than in (III) (mean 35°) or in bis(1,1-dimethyl-2,4,5-triphenylphosphonium)iron bis(tetrafluoroborate) (mean 47°) (Baum & Massa, 1985), but it is larger than in the phosphorin ring in (IV) which is bonded solely *via* P (15·6°). There has been some speculation about the reason for such different 'chair angles'. As the bonding in (VI) and (IV) is similar it seems to us that packing effects are responsible. The C—C distances within the phosphorin ring are equal within the e.s.d.'s [mean 1·40 (2) Å], indicating a high degree of π electron delocalization as also observed in (III) [1·41 (2) Å], (IV) [1·38 (1) Å] and in bis(2,4-dimethylpentadienyl)iron [1·41 (1) Å] (Wilson, Ernst & Cymbaluk, 1983).

The mean C—C distance in the phenyl substituents of the phosphorin ring is 1·39 (2) Å, which is expected, as are the distances in the cyclopentadienyl ring [mean 1·41 (2) Å]. The angles between the planes of the phenyl rings are 45 (1) [C(21)–26)/C(31–36)], 62 (1) and 80 (1)° [C(41–46)/C(21–26) and C(41–46)/-

C(31–36)]; the plane angles Fe, P(1), C(6)/C(1–5) and Fe, P(1), C(6)/C(1), P(1), C(6) are 91 (1) and 90 (1)° respectively. The plane of the cyclopentadienyl ring forms an angle of 41 (2)° with the C(1–5) plane of the phosphorin ring and with the phenyl rings it forms angles of 99 (2) [C(21–26)], 75 (2) [C(31–36)] and 58 (2)° [C(41–46)].

Table 2. *Bond angles* (°) *with e.s.d.'s in parentheses*

P(1)–Fe–C(11)	90·7 (7)	P(1)–C(5)–C(31)	118 (1)
Fe–P(1)–C(1)	114·3 (7)	C(1)–C(21)–C(26)	120 (2)
C(1)–P(1)–C(5)	103 (1)	C(5)–C(31)–C(32)	124 (2)
C(2)–C(1)–C(21)	122 (2)	C(5)–C(31)–C(36)	119 (2)
C(2)–C(3)–C(41)	121 (2)	C(32)–C(31)–C(36)	117 (2)
P(1)–C(5)–C(4)	116 (1)	C(11)–Fe–C(12)	94 (1)
C(1)–C(21)–C(22)	121 (2)	Fe–P(1)–C(6)	107·0 (5)
C(3)–C(41)–C(42)	118 (2)	P(1)–C(1)–C(21)	120 (1)
C(3)–C(41)–C(46)	121 (2)	C(2)–C(3)–C(4)	118 (2)
C(42)–C(41)–C(46)	122 (2)	C(3)–C(4)–C(5)	129 (2)
P(1)–Fe–C(12)	90·4 (8)	C(4)–C(5)–C(31)	122 (2)
Fe–P(1)–C(5)	114·3 (8)	C(22)–C(21)–C(26)	119 (2)
P(1)–C(1)–C(2)	117 (1)	Fe–C(11)–O(11)	176·1 (7)
C(1)–C(2)–C(3)	129 (2)	Fe–C(12)–O(12)	178·4 (7)
C(4)–C(3)–C(41)	121 (2)		

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