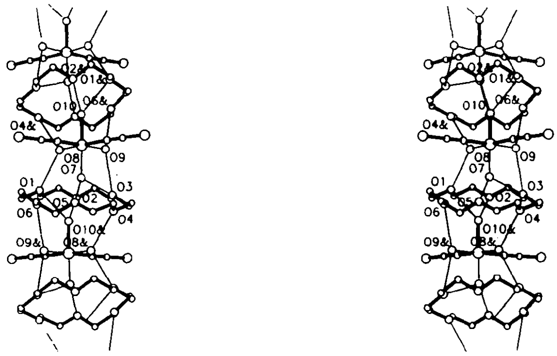

Fig. 4. Hydrogen bonding in (1).

when the size of the cation is too large to fit into the ligand cavity, the hexaether preserves the D_{3d} symmetry practically unchanged, while the cation adjusts its position out on one side of the ring. Thus the cations Rb^+ and Cs^+ are displaced respectively by 1·19 and 1·44 Å from the mean plane of the hexagon. This is also what we observe here for the $Ba(SCN)_2$ complex (2). The crown ether approximates D_{3d} symmetry with all torsion angles about C—C bonds close to 65° and those about C—O close to 180°. The ligating ether O atoms are above and below their mean plane by about 0·1–0·2 Å and the Ba^{2+} lies 0·59 Å out of this plane (Roberts & Sheldrick, 1975). The cation, also coordinated by the two N atoms of the anions on one side and the O of the water molecule on the opposite side of the ring, is displaced from the equatorial plane towards the thiocyanate anions. The Ba···O distances range from 2·808 (6) to 2·875 (5) Å with an average value of 2·834 (6) Å which corresponds to the sum of the ionic and van der Waals radii (1·47 + 1·40 = 2·87 Å) (Shannon, 1976; Pauling, 1960). The O···O distances ranging from 2·734 (9) to 2·835 (9) Å, average 2·786 (9) Å, are slightly shorter than those observed for (1).

There are no obvious linkages between the $Ba(SCN)_2$.18-crown-6.H_2O complex units.

Table 5. *Hydrogen bonds* (Å) *in* (1)

	O···O	H···O
O(7)–H(7)···O(3^{i})	2·939 (8)	2·09 (2)
O(7)–H(7')···O(5^{i})	2·792 (8)	2·10 (2)
O(9)–H(9)···O(3^{i})	2·984 (8)	2·23 (2)
O(9)–H(9')···O(6^{ii})	2·967 (8)	2·04 (2)
O(8)–H(8)···O(4^{ii})	2·914 (8)	1·86 (2)
O(8)–H(8')···O(1^{i})	2·952 (8)	2·22 (2)
O(10)···O(2^{ii})	2·742 (8)	
O(10)···O(1^{ii})	2·910 (8)	

Symmetry code: (i) x, y, z; (ii) $1-x, -y, 0{\cdot}5+z$.

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Structure of [*N,N*-Bis(diphenylphosphino)ethylamine]tricarbonyliron

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Abstract. $[Fe(C_{26}H_{25}NP_2)(CO)_3]$, $M_r = 553{\cdot}32$, monoclinic, $C2/c$, $a = 35{\cdot}741\,(8)$, $b = 10{\cdot}008\,(2)$, $c = 15{\cdot}049\,(2)$ Å, $\beta = 95{\cdot}72\,(1)°$, $V = 5356{\cdot}2$ Å^3, $Z = 8$, $D_m = 1{\cdot}368$, $D_x = 1{\cdot}372$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}706$ mm^{-1}, $F(000) = 2288$, $R = 0{\cdot}083$ ($wR = 0{\cdot}045$) for 4696 unique reflections (none

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omitted) and 335 parameters. The coordination geometry is intermediate between trigonal bipyramidal and square pyramidal, tending slightly more to the former than in the analogous structure containing a diphenylphosphinomethane ligand.

Introduction. The presence of electron-rich metal centres is considered to be essential for the reactivity of catalysts, and a programme is being undertaken to synthesize transition-metal complexes with ligands containing P as donor atom (see *e.g.* De Leeuw *et al.*, 1984). Diphosphorus ligands of type R_2PXPR_2 are being used, where R is an alkyl or aryl group and X is CH_2 or NC_2H_5, the particular interest being the effect of the nature of group X in enhancing the reactivity of the metal centres.

Experimental. Reaction of equimolar amounts of the ligand $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$, abbreviated L, and $Fe_2(CO)_9$ under photochemical conditions gave a red complex $Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}L)$ as the major product, as established by IR spectroscopy. However, recrystallization of the red complex from a toluene solution yielded yellow crystals. IR and chemical analysis showed the compound to be the mononuclear complex $Fe(CO)_3L$.

The space group was determined as *Cc* or *C*2/*c* by Weissenberg photography. The density was determined by flotation in caesium chloride solution. The number of formula units per cell was found to be eight, which made the space group *C*2/*c* appear more likely than space group *Cc* with only four asymmetric units per cell. This assumption was confirmed by the solution of the structure in *C*2/*c*. Accurate cell parameters were determined from the setting angles of 24 reflections in the range $16 < \theta < 17°$ using graphite-monochromated Mo *Kα* radiation. Intensities of 5665 reflections from a crystal of size 0·35 × 0·35 × 0·20 mm were measured out to $\theta = 25°$ ($-41 \leq h \leq 42$, $0 \leq k \leq 11$, $0 \leq l \leq 17$) on a Nonius CAD-4 diffractometer using an ω–2θ scan, scan range $\Delta\omega = (0{\cdot}44 + 0{\cdot}35\tan\theta)°$, an aperture of height 4 mm and width ($1{\cdot}16 + 1{\cdot}05\tan\theta$) mm, a final acceptance limit of 20σ at 20° min^{-1} in ω and a maximum recording time of 40 s. Three reflections (24,4,2, 10,2,10, 468) were measured every hour to monitor crystal stability and were recentred after every hundred measured reflections to monitor crystal orientation. No significant intensity changes were noted. An empirical absorption correction was made using ψ scans of eight reflections near $\chi = 90°$, transmission factors 91·35–99·78%. The structure was solved by Patterson methods and refined using the program *SHELX*76 (Sheldrick, 1976). The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + g|F_o|]^{-1}$ and $g = 0{\cdot}0001$. Atomic scattering factors were from *International Tables for X-ray Crystallography* (1974). Non-H atoms were refined anisotropically. H atoms were set to ride on the C atoms, the CH_3 group being allowed to rotate as a rigid group. H atoms were assigned isotropic temperature factors constrained to be equal in the same ring or group. The group temperature factors obtained were (in Å^2): phenyl groups – (1) 5·75, (2) 7·75, (3) 5·76, (4) 7·23; CH_2 group – 5·52; CH_3 group – 6·21. The number of parameters thus refined was 335. The refinement was taken to completion, the maximum shift/e.s.d. ratio being 0·43 for a rotation parameter of the CH_3 group. Final atomic parameters are given in Table 1.* Max./min. values on $\Delta\rho$ map were 0·93 and $-1{\cdot}64$ e Å^{-3}.

Table 1. *Fractional atomic coordinates* (× 10^5, *for* H × 10^4) *and temperature factors* (Å^2)

Equivalent anisotropic temperature factors are given for those atoms refined anisotropically. The methyl H atoms were refined as a rigid group and their isotropic temperature factors constrained to be equal.

	x	y	z	B_{eq},B(Å^2)
Fe	14768 (1)	21910 (3)	24783 (2)	3·04
P(1)	13231 (2)	2096 (6)	29475 (4)	2·77
P(2)	12283 (2)	24043 (6)	37510 (4)	2·97
N	11268 (5)	7702 (18)	38745 (12)	2·85
C(1)	17082 (8)	15435 (28)	15874 (20)	4·10
O(1)	18648 (6)	11159 (24)	10191 (15)	6·45
C(2)	11067 (8)	29946 (28)	18063 (18)	4·16
O(2)	8777 (6)	35402 (23)	13542 (16)	6·31
C(3)	18711 (8)	31587 (27)	28757 (17)	3·83
O(3)	21223 (6)	38336 (21)	31216 (5)	5·70
C(81)	10578 (7)	325 (26)	46907 (16)	3·53
C(82)	7173 (8)	−8833 (29)	45805 (20)	4·84
H(82)	698	−1399	5205	6·21
H(84)	742	−1604	4056	6·21
H(85)	467	−290	4422	6·21
C(11)	16667 (7)	−10611 (24)	33297 (16)	3·12
C(12)	15651 (8)	−22881 (26)	36650 (19)	4·09
C(13)	18375 (9)	−31976 (31)	39810 (21)	4·93
C(14)	22123 (9)	−28981 (32)	39681 (21)	4·85
C(15)	23147 (8)	−16888 (33)	36432 (21)	4·96
C(16)	20459 (7)	−7684 (28)	33202 (18)	3·83
C(31)	9450 (7)	−7073 (25)	23003 (15)	2·98
C(32)	6001 (7)	−646 (30)	21603 (18)	4·07
C(33)	3051 (8)	−6450 (33)	16497 (20)	4·77
C(34)	3512 (8)	−18819 (34)	12550 (20)	4·90
C(35)	6920 (9)	−25150 (30)	13742 (20)	4·58
C(36)	9926 (7)	−19238 (27)	18959 (17)	3·73
C(21)	15131 (7)	28848 (25)	47718 (17)	3·32
C(22)	14433 (8)	39753 (26)	52873 (18)	3·82
C(23)	16800 (8)	42733 (31)	60469 (20)	4·73
C(24)	19823 (9)	34847 (33)	62986 (21)	5·11
C(25)	20555 (9)	23814 (35)	57955 (23)	5·53
C(26)	18252 (8)	20817 (32)	50283 (21)	5·05
C(41)	7931 (7)	33348 (26)	37735 (17)	3·41
C(42)	4637 (8)	27368 (30)	39816 (20)	4·41
C(43)	1318 (9)	34497 (39)	39380 (24)	6·02
C(44)	1261 (10)	47617 (40)	36885 (24)	6·31
C(45)	4473 (11)	53781 (35)	34729 (26)	6·45
C(46)	7820 (9)	46738 (28)	35065 (21)	4·87

Discussion. Fig. 1 shows the atomic numbering [the phenyl rings attached to the pivot atoms C(11), C(21),

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* Lists of structure factors, anisotropic thermal parameters, and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44383 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

C(31) and C(41) are not included], bond lengths and the bond angles in the ligand ring. The analogous compound with the NC_2H_5 group replaced by CH_2 has been reported by Cotton, Hardcastle & Rusholme (1973). We refer to the two compounds as PNP and PCP in the following. PNP has Fe coordination very similar to that of PCP, being intermediate between trigonal bipyramidal (tbp) and square pyramidal (spy). Table 2 compares the coordination of the Fe atom in the two structures grouping those bond angles that are equivalent in the two idealized coordination polyhedra as was done by Cotton, Hardcastle & Rusholme (1973).

While it would be difficult to construct a scale on which to determine whether a particular molecular structure is closer to ideal tbp or spy, it is possible to compare the two molecular structures and identify which deviates more from a particular ideal configuration. It is concluded that the PNP coordination tends slightly more towards tbp and away from spy than does the PCP coordination according to the following criteria.

If one considers the tbp coordination, the angles in the trigonal plane [atoms P(1), C(2) and C(3)] deviate much less from the ideal 120° for PNP (113·4, 118·0 and 127·2° compared to 109·1, 115·7 and 134·2°), the maximum deviation being only 7 as opposed to 14°. The Fe atom is slightly further out of this plane for PNP [0·133 (2) as opposed to 0·113 (7) Å], the larger bond angle P(1)—Fe—C(3) of 134·2° for PCP allowing the Fe atom to move closer to the P(1),C(2),C(3) plane than for PNP.

For both molecules the Fe—C(1) bond is almost perpendicular to the P(1),C(2),C(3) plane while the Fe—P(2) bond is far from perpendicular to this plane owing to the large deviation of the P(1)—Fe—P(2) bond angle from 90°. Again PNP proves to be a slightly better tbp structure in that the angle between the two axial bonds is closer to 180° than for PCP (162·9 compared to 161·0°).

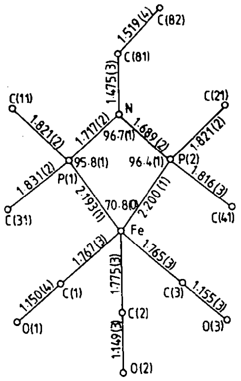

Fig. 1. Atomic numbering and selected bond lengths (Å) and angles (°). The phenyl rings attached to the pivot atoms C(11), C(21), C(31) and C(41) are not shown.

Table 2. Fe-*coordination geometry* (°) *for the two complexes with ligands based on ethylamine* (*PNP*) *and methane* (*PCP*)

		PNP	PCP
Coordination angles			
Tbp: apex to trigonal plane	P(1)–Fe–P(2)	70·8 (0)	73·5 (1)
	C(2)–Fe–P(2)	96·3 (1)	99·2 (3)
	C(3)–Fe–P(2)	91·7 (1)	89·8 (3)
	P(1)–Fe–C(1)	93·7 (1)	92·3 (3)
	C(2)–Fe–C(1)	96·5 (1)	97·3 (4)
	C(3)–Fe–C(1)	92·3 (1)	91·6 (4)
Tbp: trigonal plane	P(1)–Fe–C(2)	113·4 (1)	109·1 (3)
	C(2)–Fe–C(3)	118·0 (1)	115·7 (4)
	P(1)–Fe–C(3)	127·2 (1)	134·2 (3)
Spy: apex to basal plane	P(1)–Fe–C(2)	113·4 (1)	109·1 (3)
	P(2)–Fe–C(2)	96·3 (1)	99·2 (3)
	C(1)–Fe–C(2)	96·5 (1)	97·3 (4)
	C(3)–Fe–C(2)	118·0 (1)	115·7 (4)
Spy: basal plane	C(1)–Fe–C(3)	92·3 (1)	91·6 (4)
	C(3)–Fe–P(2)	91·7 (1)	89·8 (3)
	P(2)–Fe–P(1)	70·8 (0)	73·5 (1)
	P(1)–Fe–C(1)	93·7 (1)	92·3 (3)
Angles in the ligand ring [X = N for PNP and X = C(4) for PCP]			
Bond angles	P(1)–Fe–P(2)	70·8 (0)	73·5 (1)
	Fe–P(1)–X	95·8 (1)	97·9 (2)
	Fe–P(2)–X	96·4 (1)	97·6 (2)
	P(1)–X–P(2)	96·7 (1)	90·8 (2)
Dihedral angles	Fe–P(1)–X–P(2)	−3·5 (1)	−3·9 (2)
	P(1)–X–P(2)–Fe	3·5 (1)	3·9 (2)
	X–P(2)–Fe–P(1)	−2·9 (1)	−3·4 (2)
	P(2)–Fe–P(1)–X	2·9 (1)	3·4 (2)

With reference to ideal spy coordination the PNP coordination deviates further from this than for PCP. The angles between the bonds to the apex atom C(2) and to atoms in the basal plane differ more from each other than for PCP, the range of values being 21·7° for PNP and only 18·4° for PCP, and the puckering of the basal plane is more marked for PNP. In the basal plane the range of values of angles subtended at the Fe atom is also larger for PNP (22·9 as opposed to 18·8°) owing to the smaller P(1)—Fe—P(2) angle in PNP (70·8 compared to 73·5°).

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