Chlorido(2-iminomethyl-3-fluorophenyl-κ^2C^1,*N*)tris(trimethylphosphane-κP)iron

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The title compound, [Fe(C$_7$H$_5$FN)Cl(C$_3$H$_9$P)$_3$], was obtained as a product of the reaction of [Fe(Me$_3$P)$_4$] with a molar equivalent of (2-chloro-6-fluorophenyl)methanimine in diethyl ether. This compound is sensitive to air, and rapidly decomposes when exposed to air for a few minutes. The Fe atom has an octahedral coordination geometry in which the bidentate fluorophenyl methanimine ligand forms the equatorial plane with the Cl atom and one of the trimethylphosphane ligands. The other two trimethylphosphane ligands are located in the axial positions. In the crystal, an N—H···Cl hydrogen bond occurs.

Related literature

For related literature regarding C—Cl bond activation, see: Wang *et al.* (2007); Wang & Love (2008); Shi *et al.* (2009). Related crystal structures of iron compounds have not yet been reported in the literature. For substituted phenyl-methanimine coordinated dihydride complexes of osmium, see: Schloerer *et al.* (2006); Barea *et al.* (1998).
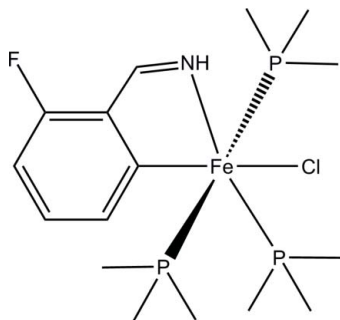
Experimental

Crystal data

[Fe(C$_7$H$_5$FN)Cl(C$_3$H$_9$P)$_3$]	V = 2146.4 (2) Å^3
M_r = 441.64	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 8.9879 (6) Å	μ = 1.06 mm^{-1}
b = 19.4457 (13) Å	T = 298 K
c = 13.5438 (7) Å	0.20 × 0.18 × 0.15 mm
β = 114.937 (3)°	

Data collection

Bruker APEXII CCD diffractometer	12499 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)	4859 independent reflections
$T_{\min}$ = 0.816, $T_{\max}$ = 0.858	4109 reflections with $I > 2\sigma(I)$
	R_{int} = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029	217 parameters
$wR(F^2)$ = 0.071	H-atom parameters constrained
S = 1.04	$\Delta\rho_{\max}$ = 0.37 e Å^{-3}
4859 reflections	$\Delta\rho_{\min}$ = −0.23 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl1^i	0.86	2.53	3.3339 (15)	157

Symmetry code: (i) $-x, -y + 1, -z + 1$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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supporting information

Chlorido(2-iminomethyl-3-fluorophenyl-*κ²C¹,N*)tris(trimethylphosphane-*κP*)iron

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S1. Comment

C-Cl bond activation and C-C coupling reactions are of great interest, with much focus on ortho-substitued imines (Wang *et al.*, 2007; Wang & Love, 2008), where Pt complexes have been used to catalyze the cross coupling of imines and dimethylzinc reagents through C-X bond activation. We have previously shown that the iron complexes supported by trimethylphosphine can easily activate the C-X (X=Cl,F) bond (Shi *et al.*, 2009).

Reaction of the low valent complex of $Fe(PMe_3)_4$ with (2-chloro-6-fluorophenyl)methanimine afforded the title compound. The *ortho* C—Cl bond was selectively activated due to its energy being lower than the C—F bond. The coordination of the imine group and one of the C atoms led to the formation of a five membered chelate ring which can provide enough energy to actiatve the C—Cl bond. It indicates that with the assistance of the imine group iron(0) complexes can easily activate the C—Cl bond affording iron(II) chloride complexes. Subsequently, C—C coupling reactions with organometallic reagents may occur.

In the title molecule (Fig. 1) the iron atom lies in an octahedral geometry in which atoms C1, N1, Cl1 and P2 form the basal plane with P1 and P3 in the axial positions. The two axial groups are located in a distorted linear geometry. A five-membered chelate ring is formed by C1, C6, C7, N1 and Fe. The bite angle of N1—Fe—C1 is 81.08 (7)°. The sum of internal bond angles (360.0 °) of N1—Fe—C1, C1—Fe—P2, P2—Fe—Cl1 and Cl1—Fe—N1 indicates nearly perfect planarity. The N—H···Cl interaction is rather short (2.53 Å). The probable reason is the steric effect of atom P2 which forces the Cl1 atom closer to the H1 atom. The C1—Fe—Cl1 angle is 167.34 (5)°, while the N1—Fe—Cl1 angle (86.27 (4)°) is less than 90°. Related structures of Os complexes containing the same iminomethyl ligand have been reported in the literature (Barea *et al.*, 1998; Schloerer *et al.*, 2006), although one molecule of hydrogen occupies the position *trans* to the nitrogen atom instead of one of the trimethylphosphine ligands. In this structure the N—Os—Cl angle is also less than 90°, and also contains a similar short N—H···Cl interaction.

S2. Experimental

A sample of $Fe(PMe_3)_4$ (0.50 g, 1.39 mmol) in 30 ml of diethyl ether was combined with a solution of (2-chloro-6-fluorophenyl)methanimine (0.22 g, 1.39 mmol) in diethyl ether (20 ml) at -80 °. The reaction mixture was warmed to ambient temperature and stirred for 24 h to form a red solution. The volatiles were removed *in vacuo*, and the resulting solid was extracted with pentane (40 ml). Crystallization at -15 ° afforded red crystals suitable for X-ray diffraction analysis (yield 0.40 g, 65%), dec. > 86 °.

S3. Refinement

All H atoms on C were placed in calculated positions with a C—H bond distance of 0.93 or 0.96 Å and $U_{iso}(H) = 1.2U_{eq}$ of the carrier atom.
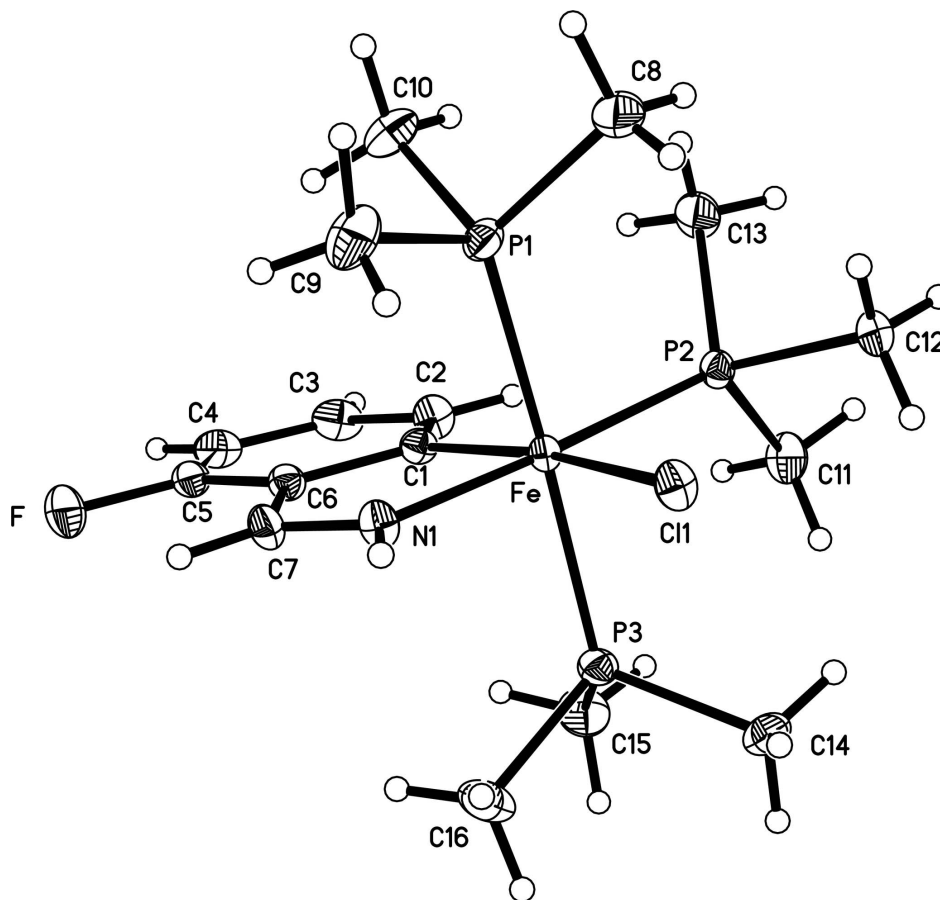
Figure 1

A view of the structure of (I), showing the atomic numbering scheme and 30% probability displacement ellipsoids.

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Crystal data

[Fe(C$_7$H$_5$FN)Cl(C$_3$H$_9$P)$_3$]	$F(000) = 928$
$M_r = 441.64$	$D_x = 1.367$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P2ybc	Cell parameters from 5013 reflections
$a = 8.9879$ (6) Å	$\theta = 2.5–27.5°$
$b = 19.4457$ (13) Å	$\mu = 1.06$ mm^{-1}
$c = 13.5438$ (7) Å	$T = 298$ K
$\beta = 114.937$ (3)°	Block, red
$V = 2146.4$ (2) Å^3	$0.20 \times 0.18 \times 0.15$ mm
$Z = 4$	

Data collection

Bruker APEXII CCD diffractometer	Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
Radiation source: fine-focus sealed tube	$T_{min} = 0.816$, $T_{max} = 0.858$
Graphite monochromator	12499 measured reflections
φ and ω scans	4859 independent reflections
	4109 reflections with $I > 2\sigma(I)$

$R_{int} = 0.024$

$\theta_{max} = 27.5°$, $\theta_{min} = 2.0°$

$h = -10 \rightarrow 11$

$k = -24 \rightarrow 25$

$l = -17 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.029$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.071$	
$S = 1.04$	H-atom parameters constrained
4859 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0334P)^2 + 0.4204P]$
217 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} = 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.37$ e Å^{-3}
	$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Fe	0.02988 (3)	0.391645 (11)	0.325636 (18)	0.01883 (7)
P3	0.25510 (6)	0.35114 (2)	0.46464 (4)	0.02733 (11)
P2	0.14694 (5)	0.39138 (2)	0.20985 (4)	0.02377 (11)
P1	−0.19959 (5)	0.44130 (2)	0.20154 (4)	0.02855 (11)
C1	−0.0641 (2)	0.29926 (8)	0.29408 (13)	0.0239 (3)
C6	−0.1656 (2)	0.28469 (9)	0.34912 (13)	0.0249 (4)
C5	−0.2479 (2)	0.22233 (10)	0.33495 (15)	0.0311 (4)
C4	−0.2322 (2)	0.17074 (10)	0.27239 (15)	0.0377 (5)
H4	−0.2877	0.1293	0.2647	0.045*
C3	−0.1304 (3)	0.18198 (9)	0.22048 (15)	0.0372 (5)
H3	−0.1154	0.1472	0.1784	0.045*
C2	−0.0503 (2)	0.24454 (9)	0.23040 (15)	0.0319 (4)
H2	0.0153	0.2505	0.1933	0.038*
N1	−0.08235 (18)	0.39126 (7)	0.42146 (12)	0.0272 (3)
H1	−0.0735	0.4256	0.4636	0.033*
C7	−0.1695 (2)	0.33880 (9)	0.42040 (14)	0.0291 (4)
H7	−0.2296	0.3360	0.4618	0.035*
C12	0.2364 (2)	0.47338 (9)	0.19708 (15)	0.0320 (4)
H12A	0.3218	0.4860	0.2663	0.048*
H12B	0.1530	0.5082	0.1737	0.048*
H12C	0.2816	0.4690	0.1445	0.048*
C13	0.0237 (3)	0.37148 (12)	0.06515 (15)	0.0414 (5)

H13A	−0.0624	0.4048	0.0344	0.062*
H13B	−0.0233	0.3265	0.0587	0.062*
H13C	0.0925	0.3728	0.0269	0.062*
C11	0.3211 (2)	0.33487 (10)	0.22908 (17)	0.0375 (5)
H11A	0.3555	0.3428	0.1719	0.056*
H11B	0.2884	0.2877	0.2273	0.056*
H11C	0.4105	0.3445	0.2981	0.056*
C8	−0.1846 (3)	0.51567 (12)	0.1234 (2)	0.0500 (6)
H8A	−0.2926	0.5328	0.0792	0.075*
H8B	−0.1322	0.5022	0.0776	0.075*
H8C	−0.1211	0.5511	0.1725	0.075*
C10	−0.3503 (2)	0.38749 (12)	0.09655 (18)	0.0475 (6)
H10A	−0.3822	0.3504	0.1302	0.071*
H10B	−0.3030	0.3692	0.0504	0.071*
H10C	−0.4449	0.4146	0.0538	0.071*
C9	−0.3291 (3)	0.47893 (11)	0.2609 (2)	0.0479 (6)
H9A	−0.4121	0.5070	0.2075	0.072*
H9B	−0.2632	0.5067	0.3224	0.072*
H9C	−0.3803	0.4429	0.2840	0.072*
C14	0.4433 (2)	0.40139 (11)	0.50640 (17)	0.0441 (5)
H14A	0.5319	0.3771	0.5623	0.066*
H14B	0.4286	0.4451	0.5340	0.066*
H14C	0.4684	0.4084	0.4449	0.066*
C15	0.3272 (3)	0.26346 (10)	0.46240 (18)	0.0451 (5)
H15A	0.3641	0.2595	0.4057	0.068*
H15B	0.2391	0.2317	0.4491	0.068*
H15C	0.4163	0.2532	0.5313	0.068*
C16	0.2353 (3)	0.34609 (12)	0.59360 (16)	0.0458 (5)
H16A	0.3393	0.3340	0.6511	0.069*
H16B	0.1554	0.3117	0.5881	0.069*
H16C	0.2008	0.3899	0.6092	0.069*
F	−0.34624 (14)	0.21266 (6)	0.38775 (10)	0.0473 (3)
Cl1	0.11769 (5)	0.50640 (2)	0.39209 (4)	0.02803 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe	0.02089 (13)	0.01713 (12)	0.02020 (13)	−0.00157 (9)	0.01036 (10)	−0.00253 (9)
P3	0.0284 (2)	0.0237 (2)	0.0260 (2)	−0.00102 (18)	0.00766 (19)	0.00456 (18)
P2	0.0242 (2)	0.0271 (2)	0.0231 (2)	−0.00228 (18)	0.01291 (18)	−0.00302 (17)
P1	0.0204 (2)	0.0289 (2)	0.0338 (3)	0.00095 (18)	0.00892 (19)	0.00162 (19)
C1	0.0254 (8)	0.0222 (8)	0.0227 (8)	−0.0012 (7)	0.0089 (7)	−0.0011 (7)
C6	0.0263 (9)	0.0237 (8)	0.0238 (8)	−0.0022 (7)	0.0096 (7)	0.0012 (7)
C5	0.0281 (9)	0.0313 (10)	0.0288 (9)	−0.0073 (8)	0.0069 (8)	0.0074 (8)
C4	0.0423 (11)	0.0239 (9)	0.0336 (10)	−0.0110 (8)	0.0031 (9)	0.0016 (8)
C3	0.0509 (12)	0.0219 (9)	0.0315 (10)	−0.0031 (8)	0.0103 (9)	−0.0076 (8)
C2	0.0395 (10)	0.0256 (9)	0.0329 (10)	−0.0050 (8)	0.0175 (8)	−0.0085 (8)
N1	0.0347 (8)	0.0233 (7)	0.0299 (8)	−0.0039 (6)	0.0198 (7)	−0.0072 (6)

C7	0.0325 (10)	0.0324 (10)	0.0290 (9)	−0.0031 (8)	0.0194 (8)	−0.0001 (8)
C12	0.0320 (10)	0.0350 (10)	0.0337 (10)	−0.0038 (8)	0.0184 (8)	0.0030 (8)
C13	0.0455 (12)	0.0559 (13)	0.0254 (10)	−0.0109 (10)	0.0174 (9)	−0.0086 (9)
C11	0.0375 (11)	0.0365 (11)	0.0479 (12)	0.0022 (9)	0.0273 (10)	−0.0050 (9)
C8	0.0326 (11)	0.0499 (13)	0.0586 (14)	0.0082 (10)	0.0106 (10)	0.0259 (11)
C10	0.0277 (10)	0.0572 (14)	0.0437 (13)	−0.0041 (10)	0.0015 (9)	−0.0069 (10)
C9	0.0316 (11)	0.0448 (12)	0.0696 (16)	0.0098 (9)	0.0235 (11)	−0.0042 (11)
C14	0.0296 (10)	0.0465 (12)	0.0406 (12)	−0.0066 (9)	−0.0004 (9)	0.0105 (10)
C15	0.0475 (12)	0.0315 (11)	0.0546 (13)	0.0139 (9)	0.0197 (11)	0.0145 (10)
C16	0.0600 (14)	0.0450 (12)	0.0273 (10)	−0.0034 (11)	0.0135 (10)	0.0072 (9)
F	0.0466 (7)	0.0466 (7)	0.0524 (7)	−0.0150 (6)	0.0245 (6)	0.0088 (6)
Cl1	0.0366 (2)	0.01904 (19)	0.0327 (2)	−0.00468 (17)	0.01878 (19)	−0.00525 (17)

Geometric parameters (Å, º)

Fe—N1	1.9508 (14)	C7—H7	0.9300
Fe—C1	1.9544 (16)	C12—H12A	0.9600
Fe—P2	2.2265 (5)	C12—H12B	0.9600
Fe—P3	2.2470 (5)	C12—H12C	0.9600
Fe—P1	2.2556 (5)	C13—H13A	0.9600
Fe—Cl1	2.4111 (5)	C13—H13B	0.9600
P3—C14	1.825 (2)	C13—H13C	0.9600
P3—C15	1.829 (2)	C11—H11A	0.9600
P3—C16	1.832 (2)	C11—H11B	0.9600
P2—C12	1.8268 (18)	C11—H11C	0.9600
P2—C11	1.8393 (19)	C8—H8A	0.9600
P2—C13	1.8404 (19)	C8—H8B	0.9600
P1—C10	1.824 (2)	C8—H8C	0.9600
P1—C9	1.824 (2)	C10—H10A	0.9600
P1—C8	1.830 (2)	C10—H10B	0.9600
C1—C2	1.408 (2)	C10—H10C	0.9600
C1—C6	1.429 (2)	C9—H9A	0.9600
C6—C5	1.391 (2)	C9—H9B	0.9600
C6—C7	1.439 (2)	C9—H9C	0.9600
C5—C4	1.359 (3)	C14—H14A	0.9600
C5—F	1.364 (2)	C14—H14B	0.9600
C4—C3	1.386 (3)	C14—H14C	0.9600
C4—H4	0.9300	C15—H15A	0.9600
C3—C2	1.391 (3)	C15—H15B	0.9600
C3—H3	0.9300	C15—H15C	0.9600
C2—H2	0.9300	C16—H16A	0.9600
N1—C7	1.283 (2)	C16—H16B	0.9600
N1—H1	0.8600	C16—H16C	0.9600
N1—Fe—C1	81.08 (7)	C6—C7—H7	123.2
N1—Fe—P2	177.39 (5)	P2—C12—H12A	109.5
C1—Fe—P2	97.64 (5)	P2—C12—H12B	109.5
N1—Fe—P3	88.69 (5)	H12A—C12—H12B	109.5

C1—Fe—P3	90.84 (5)	P2—C12—H12C	109.5
P2—Fe—P3	93.61 (2)	H12A—C12—H12C	109.5
N1—Fe—P1	86.02 (5)	H12B—C12—H12C	109.5
C1—Fe—P1	93.18 (5)	P2—C13—H13A	109.5
P2—Fe—P1	91.794 (19)	P2—C13—H13B	109.5
P3—Fe—P1	172.79 (2)	H13A—C13—H13B	109.5
N1—Fe—Cl1	86.27 (4)	P2—C13—H13C	109.5
C1—Fe—Cl1	167.34 (5)	H13A—C13—H13C	109.5
P2—Fe—Cl1	95.022 (17)	H13B—C13—H13C	109.5
P3—Fe—Cl1	88.522 (18)	P2—C11—H11A	109.5
P1—Fe—Cl1	86.246 (18)	P2—C11—H11B	109.5
C14—P3—C15	102.46 (10)	H11A—C11—H11B	109.5
C14—P3—C16	100.56 (11)	P2—C11—H11C	109.5
C15—P3—C16	98.25 (10)	H11A—C11—H11C	109.5
C14—P3—Fe	117.51 (7)	H11B—C11—H11C	109.5
C15—P3—Fe	120.89 (7)	P1—C8—H8A	109.5
C16—P3—Fe	113.72 (8)	P1—C8—H8B	109.5
C12—P2—C11	98.76 (9)	H8A—C8—H8B	109.5
C12—P2—C13	100.02 (9)	P1—C8—H8C	109.5
C11—P2—C13	96.86 (10)	H8A—C8—H8C	109.5
C12—P2—Fe	114.99 (6)	H8B—C8—H8C	109.5
C11—P2—Fe	121.91 (7)	P1—C10—H10A	109.5
C13—P2—Fe	119.97 (7)	P1—C10—H10B	109.5
C10—P1—C9	99.88 (11)	H10A—C10—H10B	109.5
C10—P1—C8	102.37 (11)	P1—C10—H10C	109.5
C9—P1—C8	98.87 (11)	H10A—C10—H10C	109.5
C10—P1—Fe	118.72 (8)	H10B—C10—H10C	109.5
C9—P1—Fe	113.34 (8)	P1—C9—H9A	109.5
C8—P1—Fe	120.13 (7)	P1—C9—H9B	109.5
C2—C1—C6	114.22 (15)	H9A—C9—H9B	109.5
C2—C1—Fe	133.41 (14)	P1—C9—H9C	109.5
C6—C1—Fe	112.36 (12)	H9A—C9—H9C	109.5
C5—C6—C1	121.36 (16)	H9B—C9—H9C	109.5
C5—C6—C7	124.61 (16)	P3—C14—H14A	109.5
C1—C6—C7	114.01 (15)	P3—C14—H14B	109.5
C4—C5—F	119.09 (16)	H14A—C14—H14B	109.5
C4—C5—C6	122.71 (18)	P3—C14—H14C	109.5
F—C5—C6	118.19 (17)	H14A—C14—H14C	109.5
C5—C4—C3	117.68 (17)	H14B—C14—H14C	109.5
C5—C4—H4	121.2	P3—C15—H15A	109.5
C3—C4—H4	121.2	P3—C15—H15B	109.5
C4—C3—C2	120.94 (18)	H15A—C15—H15B	109.5
C4—C3—H3	119.5	P3—C15—H15C	109.5
C2—C3—H3	119.5	H15A—C15—H15C	109.5
C3—C2—C1	123.01 (18)	H15B—C15—H15C	109.5
C3—C2—H2	118.5	P3—C16—H16A	109.5
C1—C2—H2	118.5	P3—C16—H16B	109.5
C7—N1—Fe	118.71 (12)	H16A—C16—H16B	109.5

C7—N1—H1	120.6	P3—C16—H16C	109.5
Fe—N1—H1	120.6	H16A—C16—H16C	109.5
N1—C7—C6	113.67 (15)	H16B—C16—H16C	109.5
N1—C7—H7	123.2		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1[i]	0.86	2.53	3.3339 (15)	157

Symmetry code: (i) −*x*, −*y*+1, −*z*+1.