Intricacies of ligand coordination in tricarbonyl-chromium(0) complexes with *ortho*- and *para*-fluorobiphenyls

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Received 22 June 2017

Accepted 21 July 2017

Edited by D. S. Yufit, University of Durham, England

Keywords: arene–arene dihedral angles; DFT computations; crystal structure; fluorobiphenyl; fluorinated compounds; tricarbonyl-chromium(0).

CCDC references: 1563759; 1563758; 1563757; 1563756

Supporting information: this article has supporting information at journals.iucr.org/c

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The steric and electronic factors that influence which of the two rings of a substituted biphenyl ligand coordinates to chromium are of interest and it has been suggested that haptotropic rearrangements within these molecules may be limited if the arene–arene dihedral angle is too large. Two tricarbonylchromium(0) complexes and their respective free ligands have been characterized by single-crystal X-ray diffraction. In the solid state, tricarbonyl[(1',2',3',4',5',6'- η)-2-fluoro-1,1'-biphenyl]chromium(0), [Cr(C₁₂H₉F)(CO)₃], (I), exists as the more stable isomer with the nonhalogenated arene ring ligated to the metal center. Similarly, tricarbonyl[(1',2',3',4',5',6'- η)-4-fluoro-1,1'-biphenyl]chromium(0) crystallizes as the more stable isomer with the phenyl ring bonded to the Cr⁰ center. The arene–arene dihedral angles in these complexes are 55.77 (4) and 52.4 (5)°, respectively. Structural features of these complexes are compared to those of the DFT-optimized geometries of ten tricarbonyl[(η^6 -C₆H₅)(4-F-C₆H₄)]chromium model complexes. The solid-state structures of the free ligands 2-fluoro-1,1'-biphenyl and 4-fluoro-1,1'-biphenyl, both C₁₂H₉F, exhibit arene–arene dihedral angles of 54.83 (7) and 0.71 (8)°, respectively. The molecules of the free ligands occupy crystallographic twofold axes and exhibit positional disorder. Weak intermolecular C–H...F interactions are observed in all four structures.

1. Introduction

In our ongoing study of the syntheses, structures and haptotropic rearrangements of substituted (biphenyl)tricarbonylchromium compounds, we have become especially interested in steric and electronic factors that influence which of the two rings of the substituted biphenyl ligand coordinates to chromium. We have also focused our attention on the arene–arene dihedral angles in these complexes, since it has been suggested that haptotropic rearrangements within these molecules may be limited if the arene–arene dihedral angle is too large. A study describing a series of substituted (biphenyl)tricarbonylchromium compounds has suggested that a necessary condition for inter-ring haptotropic rearrangement is an arene–arene dihedral angle less than 22°, as determined either by calculation or by single-crystal X-ray crystallography (Oprunenko, 2000). Inter-ring steric hindrance effected by a nonhydrogen substituent in the *ortho* position has been shown to twist the arene rings out of coplanarity, in some cases, to a great enough degree to prevent the metal from migrating between rings.

We report here the solid-state structures of the isomeric compounds tricarbonyl[(1',2',3',4',5',6'- η)-2-fluoro-1,1'-biphenyl]-

Table 1
Experimental details.

	(I)	(II)	(III)	(IV)
Crystal data				
Chemical formula	$[\text{Cr}(\text{C}_{12}\text{H}_9\text{F})(\text{CO})_3]$	$[\text{Cr}(\text{C}_{12}\text{H}_9\text{F})(\text{CO})_3]$	$\text{C}_{12}\text{H}_9\text{F}$	$\text{C}_{12}\text{H}_9\text{F}$
M_r	308.22	308.22	172.19	172.19
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Orthorhombic, $Fdd2$	Orthorhombic, $Pbcn$
Temperature (K)	100	120	100	100
a, b, c (Å)	7.0166 (3), 27.4725 (11), 7.1101 (3)	7.0616 (5), 28.3503 (19), 7.0571 (4)	12.9824 (9), 23.0588 (15), 5.7527 (4)	5.6462 (14), 20.739 (5), 7.292 (2)
α, β, γ (°)	90, 113.738 (1), 90	90, 114.324 (5), 90	90, 90, 90	90, 90, 90
V (Å ³)	1254.61 (9)	1287.40 (15)	1722.1 (2)	853.9 (4)
Z	4	4	8	4
Radiation type	Mo $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	0.93	7.48	0.74	0.09
Crystal size (mm)	$0.4 \times 0.34 \times 0.14$	$0.66 \times 0.31 \times 0.16$	$0.56 \times 0.14 \times 0.02$	$0.39 \times 0.11 \times 0.03$
Data collection				
Diffractometer	Bruker SAINT CCD area detector	Bruker APEXII CCD	Bruker SMART APEXII	Bruker APEXII Quazar
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
$T_{\min}, T_{\max}$	0.708, 0.881	0.083, 0.381	0.671, 0.754	0.706, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	20790, 2571, 2421	19716, 2520, 2479	7085, 836, 825	19177, 1055, 899
R_{int}	0.021	0.039	0.028	0.029
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.625	0.618	0.620	0.667
Refinement				
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.024, 0.068, 1.07	0.028, 0.077, 1.09	0.039, 0.107, 1.13	0.045, 0.143, 1.11
No. of reflections	2571	2520	836	1055
No. of parameters	181	181	64	68
No. of restraints	0	0	1	1
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.39, -0.20	0.30, -0.39	0.36, -0.16	0.45, -0.16
Absolute structure	—	—	Flack x determined using 351 quotients $[(I^+) - (I^-)]/[I^+ + (I^-)]$ (Parsons <i>et al.</i> , 2013)	—
Absolute structure parameter	—	—	-0.07 (17)	—

Computer programs: SMART (Bruker, 2003), APEX3 (Bruker, 2016), SAINT (Bruker, 2003), SAINT-Plus (Bruker, 2016), SHELXS97 (Sheldrick, 2008), SHELXT (Sheldrick, 2015a), SHELXL2016 (Sheldrick, 2015b) and OLEX2 (Dolomanov *et al.*, 2009).

chromium(0), $[(\eta^6\text{-C}_6\text{H}_5)(2\text{-F-C}_6\text{H}_4)]\text{Cr}(\text{CO})_3$, (I), and tricarbonyl $[(1',2',3',4',5',6'\text{-}\eta)\text{-4-fluoro-1,1'-biphenyl}]\text{chromium}(0)$, $[(\eta^6\text{-C}_6\text{H}_5)(4\text{-F-C}_6\text{H}_4)]\text{Cr}(\text{CO})_3$, (II), and of their respective free ligands 2-fluoro-1,1'-biphenyl or *ortho*-F-C₆H₄-Ph, (III), and 4-fluoro-1,1'-biphenyl or *para*-F-C₆H₄-Ph, (IV). Our intention in preparing the metal complexes was first to explore how the steric and electronic effects of a fluorine substituent on the biphenyl ligand would influence ring selectivity of chromium coordination. Regarding steric effects, it seemed reasonable to expect that during the syntheses of (biphenyl)-tricarbonylchromium compounds, steric hindrance imparted by multiple substituents on one of the biphenyl rings might decrease the propensity of that ring to coordinate to chromium. We wondered if the small size of fluorine might reduce this effect. Regarding electronic effects, it was believed that a ring that bears a highly electronegative substituent would be electron-poor and less likely to coordinate to chromium. Although fluorine is highly electronegative, there are cases where it is known to act as a π -donor. Some examples of this are indicated by the *ortho/para*-directing nature of fluorine in electrophilic aromatic substitution (Carey & Giuliano, 2014),

the -0.03 value of the σ^- parameter used for fluorine in the Hammett equation (Ritchie, 1964), and fluorine π -donor characteristics that have been described in structures such as $(\eta^6\text{-C}_6\text{H}_5\text{F})\text{Cr}(\text{CO})_3$ (Zeller *et al.*, 2004).

Scheme 1

2. Experimental

2.1. Synthesis and crystallization

Compounds (I) and (II) were synthesized according to the method of Mahaffy & Pauson (1990) by heating a butyl ether/tetrahydrofuran solution of hexacarbonylchromium for 24 h with 2-fluorobiphenyl in the case of (I) and with 4-fluorobiphenyl in the case of (II). Details of the synthesis, purifica-

tion, and spectroscopic characterization are provided below. Recrystallization from a 3:1 (v/v) hexane–ether solution of (I) or (II) led to the formation of single crystals suitable for crystallographic analysis. The free ligands *ortho*-F-C₆H₄-Ph, (III), and *para*-F-C₆H₄-Ph, (IV), were purchased from Acros Organics and MilliporeSigma; their crystals were grown by sublimation in a round-bottomed flask. NMR spectra were obtained on a Bruker AC300 spectrometer (¹H NMR at 300 MHz and ¹³C NMR at 75 MHz) and a Bruker Avance III 400 spectrometer (¹H NMR at 400 MHz and ¹³C NMR at 100 MHz). Solution IR spectra were recorded on a MIDAC Prospect-IR PRS-102 using CsI solution cells.

2.1.1. Preparation of [(η^6 -C₆H₅)(2-F-C₆H₄)]Cr(CO)₃, (I). A mixture of hexacarbonylchromium (0.510 g, 2.32 mmol) and 2-fluorobiphenyl (0.390 g, 2.26 mmol) in butyl ether (30 ml) and tetrahydrofuran (3 ml) was degassed and heated under reflux for 24 h under a nitrogen atmosphere. Tetrahydrofuran, butyl ether, and the remaining unreacted hexacarbonylchromium were removed by vacuum distillation. Purification of the remaining yellow residue by column chromatography [silica gel, 2:1 (v/v) hexane–diethyl ether] gave a yellow band from which (I) was isolated as a yellow air-stable solid (yield 0.188 g, 27.0%; m.p. 417–420 K). ¹H NMR (CDCl₃, 300 MHz): δ 7.08–7.52 (4H, *m*, aryl), 5.88 (2H, *d*, ³*J*_{HH} = 6.1 Hz, metal-bound aryl), 5.61 (3H, *m*, metal-bound aryl). ¹³C{¹H} NMR (CDCl₃, 75 MHz): δ 218.1 (CO), 161.0 (¹*J*_{CF} = 250.1 Hz), 130.9 (²*J*_{CF} = 21.7 Hz), 130.7 (³*J*_{CF} = 9.2 Hz), 130.4 (³*J*_{CF} = 9.2 Hz), 124.9 (⁴*J*_{CF} = 3.9 Hz), 116.5 (²*J*_{CF} = 21.7 Hz), 104.9, 94.7, 92.3, 91.5. IR (CH₂Cl₂, CsI): 1970, 1895 cm^{−1}.

Scheme 2

2.1.2. Preparation of [(η^6 -C₆H₅)(2-F-C₆H₄)]Cr(CO)₃, (II). A mixture of hexacarbonylchromium (0.495 g, 2.25 mmol) and 4-fluorobiphenyl (0.385 g, 2.24 mmol) in butyl ether (30 ml) and tetrahydrofuran (3 ml) was degassed and heated under reflux for 24 h under a nitrogen atmosphere. Tetrahydrofuran, butyl ether, and the remaining unreacted hexacarbonylchromium were removed by vacuum distillation. Purification of the remaining yellow residue by column chromatography [silica gel, 2:1 (v/v) hexane/diethyl ether] gave a yellow band from which (II) was isolated as a yellow air-stable solid (yield 0.151 g, 21.9%; m.p. 386–389 K). ¹H NMR (CDCl₃, 400 MHz): δ 7.48 (*dd*, ³*J*_{HH} = 7.8, ⁴*J*_{HF} = 5.3 Hz, 2H, aryl), 7.11 (*dd*, ³*J*_{HF} = 8.3, ³*J*_{HH} = 7.8 Hz, 2H, aryl), 5.63 (2H, *d*, ³*J*_{HH} = 6.1 Hz, metal-bound aryl), 5.50 (2H, *tr*, ³*J*_{HH} = 6.1 Hz, metal-bound aryl), 5.34 (1H, *tr*, ³*J*_{HH} = 6.1 Hz, metal-bound aryl). ¹³C{¹H} NMR (CDCl₃, 100 MHz): δ 232.6 (CO), 163.2 (¹*J*_{CF} = 249.2 Hz), 132.6 (⁴*J*_{CF} = 2.8 Hz), 128.9 (³*J*_{CF} = 8.5 Hz), 115.9 (²*J*_{CF} = 21.9 Hz), 109.6, 92.7, 91.9, 91.3. IR (CH₂Cl₂, CsI): 1972, 1900 cm^{−1}.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The molecule of *ortho*-F-C₆H₄-Ph, (III), resides on a twofold axis and the F atom is thereby disordered equally over two positions, as is the corresponding H atom. The molecule of *para*-F-C₆H₄-Ph, (IV), also resides on a twofold axis that contains the arene–arene bond. The F atom is disordered over the two *para* positions, with the major component contribution being 78.9 (2)%. The C1–F1 bond length to the major component is 1.3280 (17) Å, whereas the C8–F2 bond length to the minor component is suspiciously short at 1.243 (4) Å, despite an applied restraint of 1.36 (1) Å based on a search of the Cambridge Structural Database (CSD; Groom *et al.*, 2016). An unrestrained refinement produces an even shorter distance of ~1.22 Å. To ensure this was not a consequence of a systematic error, a second data set was collected on a different crystal from a different batch but the results were essentially identical, both in terms of disorder percentage and the length of the C8–F8 bond. A mass spectrometry experiment on a Thermo Q ExactiveTM Plus mass spectrometer showed a peak at *M*_r = 172, corresponding exactly to C₁₂H₉F, thereby eliminating the possibility of compositional contamination due to impurity. The origin of the abnormally short C–F bond remains unclear, and one may question the reliability of an interatomic distance determination to an atom that represents a peak of ~1.8 e Å^{−3}.

3. Results and discussion

In the syntheses of both (I) and (II), careful examination of the crude product mixtures showed that the only (biphenyl)tricarbonylchromium products which formed had the metal atom coordinated to the nonfluorinated ring. Even when shorter 15–30 min reaction times were used, product yields were very low (<10%), but analysis of the crude product mixtures still showed coordination of chromium only to the nonfluorinated ring. This might be rationalized by the high electronegativity of fluorine rendering the fluorinated ring electron-poor, but perhaps also on the basis of steric hindrance, since a fluorine substituent on the coordinated ring would be expected to exhibit additional interactions with carbonyl ligands on chromium.

Similar ring selectivity had been observed previously when 2-bromobiphenyl was heated with hexacarbonylchromium to give only the bromine analog of (I) (Czerwinski *et al.*, 2003). Conversely, when a more strongly electron-donating amino substituent was used, heating 2-aminobiphenyl or 4-aminobiphenyl with hexacarbonylchromium led to the formation of only amino-biphenyl compounds, where chromium had coordinated to the more electron-rich amino-substituted ring (Czerwinski *et al.*, 2011). We also reported that use of amide-substituted 2-acetamidobiphenyl as the coordinating ligand led to the formation of a mixture of the isomer that has chromium coordinated to the substituted ring and the isomer that has chromium coordinated to the unsubstituted ring.

Figure 1

(a) The relative energies of the ten $[(\text{C}_6\text{H}_5)(\text{F-C}_6\text{H}_4)]\text{Cr}(\text{CO})_3$ isomers in kcal mol⁻¹. The numbers correspond to the position of the lone F atom in the ligand; the F atoms are not shown. For example, $[(\eta^6\text{-C}_6\text{H}_5)(3\text{-F-C}_6\text{H}_4)]\text{Cr}(\text{CO})_3$, with the C–F vector pointing away from the carbonyl ligands, is the most stable (energy of 0.00 kcal mol⁻¹), while $[(\eta^6\text{-2-F-C}_6\text{H}_4)(\text{C}_6\text{H}_5)]\text{Cr}(\text{CO})_3$, with the C–F vector pointing away from the viewer, is the least stable, with a relative energy of 4.50 kcal mol⁻¹. (b) The torsion angles (°) between the six-membered rings. The numbers correspond to the position of the lone F atom in the ligand.

These previous results suggest that both steric and electronic factors may play a role in determining which ring of the biphenyl ligand coordinates to chromium. In the case of the syntheses of fluorinated compounds (I) and (II), it appears that any π -electron donation from fluorine is outweighed either by its steric interaction with carbonyl ligands or its high electronegativity, or both.

To corroborate our predictions, we performed density functional theory (DFT) calculations at the B3LYP/LANL2DZ level of theory on ten model $[(\text{C}_6\text{H}_5)(\text{F-C}_6\text{H}_4)]\text{Cr}(\text{CO})_3$ complexes in order to determine the most stable isomers, identify which ring has the higher propensity to ligate to the metal center, and compare the arene–arene dihedral angles between the theoretically minimized complexes and experimentally determined geometries (GAUSSIAN09; Frisch *et al.*, 2016). The theoretical results are shown in Fig. 1. The five isomers with the unsubstituted arene ring coordinated to the Cr center are more stable than complexes with the F-C₆H₄ ring bonded to the metal atom. Among the respective compounds with the *meta*-, *ortho*-, and *para*-substitution patterns, the complexes with the ligated arene ring are approximately 3 kcal mol⁻¹ more stable. The would-be equivalent *ortho*-substituted isomers differ in energy due to different positions of the F atom relative to the Cr(CO)₃ group. The same is true for the *meta*-substituted congeners. The ~31 K difference in melting points of chemical isomers (I) and (II) indicates that the latter is by far more stable. This finding contrasts with the DFT gas-phase energy calculations for the two systems that are very similar and illustrates the effect of theoretical approximations for isolated molecules.

Our second major objective was to characterize the solid-state structures of (I) and (II) by single-crystal X-ray diffraction and to compare the experimentally observed geometries with the theoretical calculations. The solid-state structure of (I) corresponds to the most stable among the four possible conformations of the model $[(\text{C}_6\text{H}_5)(\text{ortho-F-C}_6\text{H}_4)]\text{Cr}(\text{CO})_3$ system (Fig. 2a). The Cr⁰ atom exhibits a typical three-legged piano-stool geometry with expected geometrical parameters (Table 2). The C–C bond lengths in the coordinated arene ring average 1.411 (9) Å, which is 0.022 Å longer than the average bond length of 1.389 (6) Å for C–C bonds within the

Table 2

Selected geometrical parameters (Å) of complexes (I) and (II) compared to literature data.

Compound	(I)	(II)	CSD complexes*
Cr1–CO (av)	1.846 (4)	1.8432 (15)	1.798–1.855
Cr1–C(Ph)	2.2056 (14)–2.2311 (14)	2.2061 (17)–2.2316 (15)	2.195–2.265
Cr1–Centroid	1.7067 (6)	1.7067 (7)	1.707–1.728

Note: (*) eight related complexes have been considered; their CSD (Groom *et al.*, 2016) refcodes are COCRDP02 and MAJLAL (Guzei & Czerwinski, 2004), EMEYIE (Czerwinski *et al.*, 2003), EXUFAF and EXUFIN (Czerwinski *et al.*, 2011), FOZLEL (Mailvaganam *et al.*, 1987), QIQXOF (Brydges *et al.*, 2013), and ABISAI (Miles *et al.*, 2016).

noncoordinated fluorinated ring. The C–C bond lengths between the arene rings in (I)–(IV) are 1.4881 (19), 1.485 (2), 1.494 (4) and 1.4959 (19) Å, and are shorter in the Cr complexes. Interestingly, the difference in the arene–arene bond lengths in free ligand (IV) and the Cr complexes is statistically significant, whereas it is not statistically significant in the case of (III) due to the larger s.u. value.

The arene–arene dihedral angle of 55.77 (4)° in (I) is substantially larger than the theoretical value of 41.32°

Figure 2

The molecular structures of (a) (I) and (b) (II), shown with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Figure 3

The molecular structures of (a) (III) and (b) the symmetry-independent part of (III). Both structures are shown with 50% probability displacement ellipsoids. The H atom on C2 and atom F1 are 50% occupied due to positional disorder over a twofold axis perpendicular to the arene–arene bond.

(Fig. 1b), but is in good agreement with the corresponding dihedral angle of $54.83(7)^\circ$ between the arene rings in free 2-fluorobiphenyl. The dihedral angle in free 2-fluorobiphenyl is 45.82° in the DFT-minimized geometry at the B3LYP/6-311+G(d,p) level of theory (Frisch *et al.*, 2016). The ligand conformation is stabilized by weak C—H...F interactions. Atom F1 is a bifurcated acceptor of two weak C—H donors from atoms C6 and C10 of two adjacent molecules (Table 2). All four compounds exhibit C—H...F interactions that are necessarily weak due to the low acidity of the available Csp^2 —H donor bonds and the weak acceptor nature of the Csp^2 —F organic fluorines (Thalladi *et al.*, 1998).

The crystal structure of (II) corresponds to the more stable isomer between the two possible isomers for the *para*-F-substituted biphenyl (Fig. 1b), with the nonhalogenated arene ring ligating to the Cr center. Not surprisingly, the solid-state structure of (II) shows many similarities to that of (I). The geometrical parameters of this complex fall in the expected ranges (Table 2). The average C—C bond length in the coordinated arene ring is $1.411(10)$ Å, which is identical to the value found for (I), and which is 0.02 Å longer than the average bond length of $1.39(2)$ Å for C—C bonds within the noncoordinated fluorinated ring. The arene–arene dihedral angle of $52.4(5)^\circ$ is smaller than the corresponding angle of $55.77(4)^\circ$ in (I). This contrasts with the theoretical calcula-

Table 3

C—H...F and C4—H4... π interactions in the structures of (I)–(IV).

π represents the centroid of the C1–C6 ring.

Compound	Interaction	C—H...F (Å)	C...F (Å)	C—H...F ($^\circ$)
(I)	C6—H6...F1 ⁱ	2.66	3.5612 (17)	158.1
	C10—H10...F1 ⁱⁱ	2.50	3.4013 (17)	158.1
(II)	C6—H6...F1 ⁱⁱⁱ	2.48	3.122 (2)	124.8
	C8—H8...F1 ⁱⁱⁱ	2.46	3.295 (2)	146.8
(III)	C3—H3...F1 ^{iv}	2.61	3.539 (4)	165.3
	C6—H6...F1 ^v	2.65	3.548 (4)	158.6
(IV)	C4—H4... π ^{iv}	2.80	3.60	142.1
	C2—H2...F2 ^{vi}	2.67	3.291 (3)	123.8
	C7—H7...F1 ^{vii} (in plane)	2.63	3.2529 (15)	123.3
	C7—H7...F1 ^{viii} (between layers)	2.85	3.6113 (14)	137.5

Symmetry codes: (i) $x, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $x + 1, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $x + \frac{1}{2}, -y + \frac{5}{2}, z + \frac{1}{2}$; (v) $-x + 1, -y + 1, z - 1$; (vi) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (vii) $-x + \frac{1}{2}, y - 0.5, z$; (viii) $-x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$.

tions that predicted a marginally larger angle for (I) than for (II), with values of 41.32 and 38.08° , respectively (Fig. 1b). Similar to (I), compound (II) exhibits C—H...F contacts in which atom F1 participates in two hydrogen bonds (Table 3). These bonds are characterized by shorter donor–acceptor distances compared to (I), but less favorable C—H...F angles.

Most of the experimentally determined structural parameters for (I) and (II) are in good agreement with literature data (Table 2). However, the arene–arene dihedral angles in similar compounds span a wide range. This angle is 0° in μ -(η^6, η^6 -biphenyl)-bis(tricarbonylchromium) (Guzei & Czerwinski, 2004), 38.08° in (η^6 -4-aminobiphenyl)tricarbonylchromium (Czerwinski *et al.*, 2011), 60.70° in (η^6 -2-bromo-1,1'-biphenyl)tricarbonylchromium (Czerwinski *et al.*, 2003), 65.76° in (η^6 -2-aminobiphenyl)tricarbonylchromium (Czerwinski *et al.*, 2011), and $23.55(5)^\circ$ in (η^6 -biphenyl)tricarbonylchromium (Guzei & Czerwinski, 2004).

The arene–arene dihedral angle of $52.4(5)^\circ$ in (II) is surprisingly large when considering that the fluorine substituent is in the *para* position of the noncoordinated ring. In this position, it would be expected not to have significant interactions with the carbonyl ligands or with the *ortho* H atoms of the coordinated ring. By comparison, the solid-state structure of the unsubstituted analog [$(\eta^6\text{-C}_6\text{H}_5)(\text{C}_6\text{H}_5)\text{Cr}(\text{CO})_3$] exhibits a arene–arene dihedral angle of $23.55(5)^\circ$, whereas its free ligand, *i.e.* biphenyl, is planar in the solid state (Charbonneau & Delugeard, 1977). The twisting that is effected by coordination of biphenyl to $\text{Cr}(\text{CO})_3$ prompted us to examine the solid-state structures of the free ligands 2-fluorobiphenyl, (III), and 4-fluorobiphenyl, (IV). Whereas the range of observed arene–arene dihedral angles is large, the energy difference among various relative ring positions falls within a few kcal mol^{-1} and our variable-temperature NMR studies show no evidence of a significant rotational barrier about the arene–arene bond.

Whereas the structure of (III) at 293 K has been reported previously (Rajnikant *et al.*, 1995), we sought to redetermine the structure at 100 K for consistency with the conditions of our determinations of (I), (II), and (IV) (Fig. 3).

Figure 4
The molecular packing of the free ligands, showing (a) the three-dimensional framework in (III), viewed along [101], and (b) the layered structure of (IV), viewed along the *b* axis.

The structure of (III) at 100 K closely resembles the previously reported 293 K analog, but expectedly the bond lengths are slightly longer in the 100 K structure. In particular, the C2—F1 bond length of 1.331 (4) Å is in a reasonably close agreement with the previously determined value of 1.319 (4) Å, but slightly longer, as expected due to reduced librational effects at 100 K. Both values are noticeably shorter than the 1.36 Å average for related compounds in the Cambridge Structural Database (Groom *et al.*, 2016). The C—F distances in (I), (II), and (IV) are 1.3622 (17), 1.355 (2), and 1.3280 (17) Å, respectively. The arene–arene dihedral angles in (III) [54.83 (7)° at 100 K and 54 (3)° at 293 K] are quite close to the analogous angle in (I), suggesting that ligation to Cr(CO)₃ imparts little additional steric hindrance and results in only a marginal increase in the observed dihedral angle.

The structure of (III) is stabilized by weak C—H...F interactions, forming a three-dimensional framework (Fig. 4a). Atom F1 is a bifurcated acceptor of two H—C bonds from two adjacent molecules (Table 3). Additionally, there is a C4—H4... π herringbone-type interaction absent in the structure of (IV).

The solid-state structure of (IV) shows that the molecule resides on a crystallographic twofold axis containing the C4—C5 bond (Fig. 5).

The C4—C5 bond length [1.4959 (19) Å] is shorter than a single C—C bond, but without substantial multiple-bond character. This bond length is in excellent agreement with the arene–arene distance of 1.494 (4) Å observed in (III). The arene–arene dihedral angle in (IV) of 0.71 (8)° suggests that the molecule is essentially planar in the solid state.

In the crystal of (IV), molecules form corrugated sheets stacked in the *c* direction (Fig. 4b). Within the plane, the F atom in each of its positions forms two C—H...F interactions (Table 3). The corrugated layers are connected by additional weaker C7—H7...F1 interactions; thus, atom F1 participates in four weak C—H...F hydrogen bonds, *i.e.* two within the sheet plane and two to the layers above and below. Atom F2 participates in just two such nonclassical interactions, and this difference may rationalize why atom F1 is the major disorder component at 79.8 (2)%.

In light of the behavior of biphenyl, it is somewhat surprising that ligation of flat ligand (IV) to Cr(CO)₃ results in such a large dihedral angle of 52.4 (5)° in (II). This angle cannot be explained by π – π interactions, since they are absent in the structure of (II), nor can it be explained by intermolecular C—H...F hydrogen-bonding interactions because they are observed in all structures.

Interestingly, both C₂-symmetric structures of the free ligands (III) and (IV) exhibit positional disorder that is absent in (I) and (II). Thus, ligation of a fluorobiphenyl to chromium effectively discriminates between the two rings and only one ordered product is observed in the solid state for (I) and (II).

4. Conclusions

Compounds (I) and (II) exhibit relatively large arene–arene dihedral angles in the solid state. This angle in (I) may be

Figure 5
(a) The molecular structure of (IV) and (b) its symmetry-independent part. Both structures are shown with 50% probability displacement ellipsoids. In part (b), all disorder components are shown.

understood in terms of inter-ring *ortho*-F...*ortho*-H steric hindrance that was shown to be present in the free ligand (III). The large dihedral angle in (II) is more difficult to rationalize, especially since the free ligand (IV) exhibits a flat structure that is consistent with a fluorine substituent in the *para* position. The variability in arene–arene dihedral angles in a series of substituted (biphenyl)tricarbonylchromium compounds may only represent small energetic differences, and might simply be attributed to packing forces in the solid state. Further studies of related compounds may be necessary to advance a complete explanation for this observation. The method of heating fluorobiphenyl with hexacarbonylchromium led only to products (I) and (II), where chromium is coordinated to the nonfluorinated ring, but efforts are currently underway to find alternative synthetic methods for the preparation of the isomers where chromium is coordinated to the fluorinated ring. Syntheses of these molecules would allow their haptotropic rearrangements to be studied, and it is hoped that studies of their solid-state structures might further clarify how positional substitution of fluorine in the biphenyl ligand affects arene–arene dihedral angles. Unlike the solid-state structures of free ligands (III) and (IV), chromium complexes (I) and (II) exhibit no crystallographic symmetry and no positional disorder.

Acknowledgements

The purchase of the Thermo Q ExactiveTM Plus in 2015 was funded by an NIH Award to the Department of Chemistry, University of Wisconsin–Madison. We thank Dr Martha M. Vestling for acquiring the MS data.

Funding information

Funding for this research was provided by: United States Army Research Office DURIP (Defense University Research Instrumentation Program); the University of Wisconsin–La Crosse Faculty Research Grant Program; the University of Wisconsin–La Crosse Undergraduate Research Grant Program; National Institutes of Health (award No. 1S10

OD020022-1); Ministry of Education and Science of the Russian Federation (agreement No. 02.a03.21.0008).

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supporting information

Acta Cryst. (2017). C73, 638-644 [https://doi.org/10.1107/S2053229617010774]

Intricacies of ligand coordination in tricarbonylchromium(0) complexes with *ortho*- and *para*-fluorobiphenyls

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Computing details

Data collection: *SMART* (Bruker, 2003) for cze005, czerwinski10; *APEX3* (Bruker, 2016) for czerwinski13, czerwinski12. Cell refinement: *SAINT* (Bruker, 2003) for cze005, czerwinski10; *SAINT-Plus* (Bruker, 2016) for czerwinski13, czerwinski12. Data reduction: *SAINT* (Bruker, 2003) for cze005, czerwinski10; *SAINT-Plus* (Bruker, 2016) for czerwinski13, czerwinski12. Program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) for cze005, czerwinski10; *SHELXT* (Sheldrick, 2015a) for czerwinski13, czerwinski12. Program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015b) for cze005, czerwinski13, czerwinski12; *SHELXL2016* (Sheldrick, 2015a) for czerwinski10. For all structures, molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Tricarbonyl[(1',2',3',4',5',6'-*η*)-2-fluoro-1,1'-biphenyl]chromium(0) (cze005)

Crystal data

[Cr(C₁₂H₉F)(CO)₃]
 $M_r = 308.22$
 Monoclinic, $P2_1/c$
 $a = 7.0166$ (3) Å
 $b = 27.4725$ (11) Å
 $c = 7.1101$ (3) Å
 $\beta = 113.738$ (1)°
 $V = 1254.61$ (9) Å³
 $Z = 4$

$F(000) = 624$
 $D_x = 1.632$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 13200 reflections
 $\theta = 3.0$ – 26.4 °
 $\mu = 0.93$ mm⁻¹
 $T = 100$ K
 Plate, yellow
 $0.4 \times 0.34 \times 0.14$ mm

Data collection

Bruker SAINT CCD area detector
 diffractometer
 Graphite monochromator
 phi and ω scans
 Absorption correction: multi-scan
 (SADABS; Krause *et al.*, 2015)
 $T_{\min} = 0.708$, $T_{\max} = 0.881$
 20790 measured reflections

2571 independent reflections
 2421 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\max} = 26.4$ °, $\theta_{\min} = 3.0$ °
 $h = -8 \rightarrow 8$
 $k = -34 \rightarrow 34$
 $l = -8 \rightarrow 8$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.068$

$S = 1.07$
 2571 reflections
 181 parameters
 0 restraints

Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 0.6955P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = 0.003$$

$$\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$$

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cr1	0.25461 (3)	0.58849 (2)	0.64906 (3)	0.01547 (9)
F1	0.37666 (14)	0.73489 (3)	1.07416 (15)	0.0279 (2)
O1	0.49510 (17)	0.63961 (4)	0.44226 (17)	0.0293 (3)
O2	0.5439 (2)	0.50310 (5)	0.7360 (2)	0.0413 (3)
O3	−0.01617 (19)	0.54368 (4)	0.24436 (17)	0.0300 (3)
C1	0.3565 (2)	0.64130 (5)	0.9095 (2)	0.0167 (3)
C2	0.3366 (2)	0.59475 (5)	0.9828 (2)	0.0190 (3)
H2	0.450980	0.580891	1.093855	0.023*
C3	0.1477 (2)	0.56839 (5)	0.8924 (2)	0.0222 (3)
H3	0.135100	0.537237	0.944280	0.027*
C4	−0.0201 (2)	0.58829 (5)	0.7269 (2)	0.0227 (3)
H4	−0.146121	0.570447	0.665358	0.027*
C5	−0.0027 (2)	0.63495 (5)	0.6505 (2)	0.0208 (3)
H5	−0.117514	0.648641	0.539334	0.025*
C6	0.1848 (2)	0.66086 (5)	0.7399 (2)	0.0180 (3)
H6	0.197228	0.691839	0.686547	0.022*
C7	0.5553 (2)	0.66864 (5)	1.0082 (2)	0.0170 (3)
C8	0.5598 (2)	0.71474 (5)	1.0896 (2)	0.0198 (3)
C9	0.7405 (2)	0.74085 (6)	1.1899 (2)	0.0235 (3)
H9	0.736754	0.772398	1.243049	0.028*
C10	0.9282 (2)	0.71984 (6)	1.2113 (2)	0.0236 (3)
H10	1.054849	0.736997	1.280648	0.028*
C11	0.9313 (2)	0.67377 (6)	1.1317 (2)	0.0227 (3)
H11	1.059841	0.659598	1.145747	0.027*
C12	0.7465 (2)	0.64847 (5)	1.0315 (2)	0.0202 (3)
H12	0.750021	0.616957	0.977952	0.024*
C13	0.4037 (2)	0.61937 (5)	0.5220 (2)	0.0196 (3)
C14	0.4319 (3)	0.53577 (6)	0.7022 (2)	0.0259 (3)
C15	0.0890 (2)	0.56070 (5)	0.3997 (2)	0.0207 (3)

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cr1	0.01797 (14)	0.01454 (13)	0.01487 (13)	−0.00037 (8)	0.00763 (10)	−0.00078 (7)

F1	0.0240 (5)	0.0243 (5)	0.0340 (5)	0.0041 (4)	0.0101 (4)	−0.0087 (4)
O1	0.0245 (6)	0.0416 (7)	0.0245 (6)	−0.0076 (5)	0.0128 (5)	0.0009 (5)
O2	0.0579 (9)	0.0349 (7)	0.0359 (7)	0.0255 (6)	0.0240 (6)	0.0107 (5)
O3	0.0370 (6)	0.0274 (6)	0.0234 (6)	−0.0101 (5)	0.0098 (5)	−0.0077 (5)
C1	0.0194 (7)	0.0161 (6)	0.0168 (6)	0.0003 (5)	0.0097 (5)	−0.0024 (5)
C2	0.0258 (7)	0.0187 (7)	0.0146 (6)	0.0000 (5)	0.0103 (6)	−0.0013 (5)
C3	0.0315 (8)	0.0196 (7)	0.0214 (7)	−0.0052 (6)	0.0169 (6)	−0.0028 (6)
C4	0.0216 (7)	0.0266 (8)	0.0239 (7)	−0.0072 (6)	0.0133 (6)	−0.0073 (6)
C5	0.0174 (7)	0.0251 (7)	0.0212 (7)	0.0013 (5)	0.0090 (6)	−0.0037 (6)
C6	0.0199 (7)	0.0158 (6)	0.0201 (7)	0.0017 (5)	0.0100 (6)	−0.0011 (5)
C7	0.0191 (7)	0.0174 (7)	0.0141 (6)	−0.0005 (5)	0.0062 (5)	0.0012 (5)
C8	0.0205 (7)	0.0199 (7)	0.0187 (7)	0.0028 (5)	0.0074 (6)	0.0001 (5)
C9	0.0291 (8)	0.0192 (7)	0.0200 (7)	−0.0039 (6)	0.0076 (6)	−0.0016 (6)
C10	0.0222 (7)	0.0270 (8)	0.0173 (7)	−0.0069 (6)	0.0034 (6)	0.0023 (6)
C11	0.0183 (7)	0.0287 (8)	0.0198 (7)	0.0020 (6)	0.0062 (6)	0.0057 (6)
C12	0.0227 (7)	0.0197 (7)	0.0182 (7)	0.0028 (6)	0.0084 (6)	0.0022 (5)
C13	0.0169 (6)	0.0237 (7)	0.0161 (6)	0.0009 (5)	0.0044 (5)	−0.0025 (5)
C14	0.0363 (8)	0.0246 (8)	0.0197 (7)	0.0056 (7)	0.0142 (6)	0.0024 (6)
C15	0.0252 (7)	0.0173 (7)	0.0228 (7)	−0.0023 (6)	0.0128 (6)	0.0003 (6)

Geometric parameters (Å, °)

Cr1—C1	2.2311 (14)	C3—H3	0.9500
Cr1—C2	2.2115 (14)	C3—C4	1.398 (2)
Cr1—C3	2.2150 (14)	C4—H4	0.9500
Cr1—C4	2.2087 (15)	C4—C5	1.416 (2)
Cr1—C5	2.2146 (14)	C5—H5	0.9500
Cr1—C6	2.2056 (14)	C5—C6	1.403 (2)
Cr1—C13	1.8415 (15)	C6—H6	0.9500
Cr1—C14	1.8466 (16)	C7—C8	1.387 (2)
Cr1—C15	1.8487 (15)	C7—C12	1.398 (2)
F1—C8	1.3622 (17)	C8—C9	1.380 (2)
O1—C13	1.1552 (19)	C9—H9	0.9500
O2—C14	1.153 (2)	C9—C10	1.389 (2)
O3—C15	1.1521 (19)	C10—H10	0.9500
C1—C2	1.409 (2)	C10—C11	1.390 (2)
C1—C6	1.423 (2)	C11—H11	0.9500
C1—C7	1.4882 (19)	C11—C12	1.388 (2)
C2—H2	0.9500	C12—H12	0.9500
C2—C3	1.417 (2)		
C2—Cr1—C1	36.98 (5)	C3—C2—H2	119.7
C2—Cr1—C3	37.34 (5)	Cr1—C3—H3	129.9
C2—Cr1—C5	79.09 (6)	C2—C3—Cr1	71.19 (8)
C3—Cr1—C1	67.04 (5)	C2—C3—H3	120.0
C4—Cr1—C1	79.29 (5)	C4—C3—Cr1	71.33 (9)
C4—Cr1—C2	66.91 (6)	C4—C3—C2	119.91 (13)
C4—Cr1—C3	36.84 (6)	C4—C3—H3	120.0

C4—Cr1—C5	37.35 (6)	Cr1—C4—H4	129.1
C5—Cr1—C1	67.09 (5)	C3—C4—Cr1	71.82 (9)
C5—Cr1—C3	66.85 (6)	C3—C4—H4	119.9
C6—Cr1—C1	37.40 (5)	C3—C4—C5	120.23 (14)
C6—Cr1—C2	66.94 (5)	C5—C4—Cr1	71.55 (8)
C6—Cr1—C3	79.11 (5)	C5—C4—H4	119.9
C6—Cr1—C4	67.03 (5)	Cr1—C5—H5	130.1
C6—Cr1—C5	37.01 (5)	C4—C5—Cr1	71.10 (9)
C13—Cr1—C1	92.99 (6)	C4—C5—H5	120.2
C13—Cr1—C2	122.46 (6)	C6—C5—Cr1	71.15 (8)
C13—Cr1—C3	159.39 (6)	C6—C5—C4	119.68 (14)
C13—Cr1—C4	148.14 (6)	C6—C5—H5	120.2
C13—Cr1—C5	111.23 (6)	Cr1—C6—H6	128.6
C13—Cr1—C6	88.02 (6)	C1—C6—Cr1	72.27 (8)
C13—Cr1—C14	89.58 (7)	C1—C6—H6	119.6
C13—Cr1—C15	88.96 (6)	C5—C6—Cr1	71.85 (8)
C14—Cr1—C1	112.08 (6)	C5—C6—C1	120.79 (13)
C14—Cr1—C2	88.78 (6)	C5—C6—H6	119.6
C14—Cr1—C3	93.25 (6)	C8—C7—C1	121.13 (13)
C14—Cr1—C4	122.05 (7)	C8—C7—C12	116.92 (13)
C14—Cr1—C5	159.15 (6)	C12—C7—C1	121.89 (12)
C14—Cr1—C6	149.09 (6)	F1—C8—C7	118.36 (13)
C14—Cr1—C15	89.08 (7)	F1—C8—C9	118.12 (13)
C15—Cr1—C1	158.75 (6)	C9—C8—C7	123.50 (14)
C15—Cr1—C2	148.48 (6)	C8—C9—H9	120.8
C15—Cr1—C3	111.48 (6)	C8—C9—C10	118.30 (14)
C15—Cr1—C4	87.93 (6)	C10—C9—H9	120.8
C15—Cr1—C5	92.49 (6)	C9—C10—H10	119.9
C15—Cr1—C6	121.67 (6)	C9—C10—C11	120.23 (14)
C2—C1—Cr1	70.76 (8)	C11—C10—H10	119.9
C2—C1—C6	118.70 (13)	C10—C11—H11	120.0
C2—C1—C7	119.80 (13)	C12—C11—C10	120.01 (14)
C6—C1—Cr1	70.33 (8)	C12—C11—H11	120.0
C6—C1—C7	121.49 (12)	C7—C12—H12	119.5
C7—C1—Cr1	130.24 (9)	C11—C12—C7	121.04 (14)
Cr1—C2—H2	129.0	C11—C12—H12	119.5
C1—C2—Cr1	72.27 (8)	O1—C13—Cr1	178.60 (13)
C1—C2—H2	119.7	O2—C14—Cr1	179.46 (17)
C1—C2—C3	120.66 (14)	O3—C15—Cr1	179.23 (14)
C3—C2—Cr1	71.46 (8)		
Cr1—C1—C2—C3	−54.72 (12)	C3—C4—C5—Cr1	54.90 (13)
Cr1—C1—C6—C5	55.16 (12)	C3—C4—C5—C6	0.9 (2)
Cr1—C1—C7—C8	147.56 (12)	C4—C5—C6—Cr1	53.94 (12)
Cr1—C1—C7—C12	−35.26 (19)	C4—C5—C6—C1	−1.4 (2)
Cr1—C2—C3—C4	−54.13 (12)	C6—C1—C2—Cr1	53.30 (11)
Cr1—C3—C4—C5	−54.77 (13)	C6—C1—C2—C3	−1.4 (2)
Cr1—C4—C5—C6	−53.96 (12)	C6—C1—C7—C8	57.48 (19)

Cr1—C5—C6—C1	−55.36 (12)	C6—C1—C7—C12	−125.33 (15)
F1—C8—C9—C10	178.12 (13)	C7—C1—C2—Cr1	−126.06 (12)
C1—C2—C3—Cr1	55.10 (12)	C7—C1—C2—C3	179.22 (13)
C1—C2—C3—C4	1.0 (2)	C7—C1—C6—Cr1	125.84 (12)
C1—C7—C8—F1	−1.0 (2)	C7—C1—C6—C5	−179.00 (13)
C1—C7—C8—C9	177.32 (14)	C7—C8—C9—C10	−0.2 (2)
C1—C7—C12—C11	−177.31 (13)	C8—C7—C12—C11	0.0 (2)
C2—C1—C6—Cr1	−53.50 (11)	C8—C9—C10—C11	0.4 (2)
C2—C1—C6—C5	1.7 (2)	C9—C10—C11—C12	−0.4 (2)
C2—C1—C7—C8	−123.18 (15)	C10—C11—C12—C7	0.2 (2)
C2—C1—C7—C12	54.00 (19)	C12—C7—C8—F1	−178.32 (12)
C2—C3—C4—Cr1	54.06 (12)	C12—C7—C8—C9	0.0 (2)
C2—C3—C4—C5	−0.7 (2)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C6—H6 $\cdots$ F1 ⁱ	0.95	2.66	3.5612 (17)	158
C10—H10 $\cdots$ F1 ⁱⁱ	0.95	2.50	3.4013 (17)	158

Symmetry codes: (i) *x*, $-y+3/2$, $z-1/2$; (ii) *x*+1, $-y+3/2$, $z+1/2$.

Tricarbonyl[(1',2',3',4',5',6'- η)-4-fluoro-1,1'-biphenyl]chromium(0) (czerwinski10)

Crystal data

[Cr(C₁₂H₉F)(CO)₃]

M_r = 308.22

Monoclinic, *P*2₁/*c*

a = 7.0616 (5) Å

b = 28.3503 (19) Å

c = 7.0571 (4) Å

β = 114.324 (5)°

V = 1287.40 (15) Å³

Z = 4

F(000) = 624

D_x = 1.590 Mg m^{−3}

Cu *K*α radiation, λ = 1.54178 Å

Cell parameters from 9875 reflections

θ = 3.1–71.7°

μ = 7.48 mm^{−1}

T = 120 K

Block, yellow

0.66 × 0.31 × 0.16 mm

Data collection

Bruker APEXII CCD

diffractometer

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(SADABS; Krause *et al.*, 2015)

*T*_{min} = 0.083, *T*_{max} = 0.381

19716 measured reflections

2520 independent reflections

2479 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.039

$\theta_{\max}$ = 72.4°, $\theta_{\min}$ = 3.1°

h = −8→8

k = −34→33

l = −8→8

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.028

wR(*F*²) = 0.077

S = 1.09

2520 reflections

181 parameters

0 restraints

Hydrogen site location: inferred from

neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.040P)^2 + 0.8185P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$$

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cr1	0.24469 (4)	0.08560 (2)	0.14453 (4)	0.01430 (10)
F1	1.0904 (2)	0.23850 (5)	0.7983 (2)	0.0457 (4)
O1	0.4870 (2)	0.13494 (5)	-0.0586 (2)	0.0305 (3)
O2	0.5257 (3)	0.00166 (6)	0.2294 (2)	0.0453 (4)
O3	-0.0315 (2)	0.04327 (5)	-0.2657 (2)	0.0306 (3)
C1	0.3515 (3)	0.13767 (6)	0.4048 (2)	0.0159 (3)
C2	0.3381 (3)	0.09256 (6)	0.4825 (3)	0.0191 (3)
H2	0.455869	0.079641	0.593405	0.023*
C3	0.1510 (3)	0.06625 (6)	0.3973 (3)	0.0231 (4)
H3	0.143228	0.036093	0.452306	0.028*
C4	-0.0218 (3)	0.08472 (6)	0.2324 (3)	0.0250 (4)
H4	-0.146809	0.066977	0.174633	0.030*
C5	-0.0115 (3)	0.12983 (6)	0.1507 (3)	0.0222 (4)
H5	-0.129418	0.142450	0.038919	0.027*
C6	0.1743 (3)	0.15576 (6)	0.2360 (3)	0.0182 (3)
H6	0.181558	0.185846	0.180030	0.022*
C7	0.5471 (3)	0.16526 (6)	0.4991 (2)	0.0165 (3)
C8	0.5428 (3)	0.21124 (6)	0.5691 (3)	0.0228 (4)
H8	0.413670	0.225397	0.547814	0.027*
C9	0.7261 (3)	0.23633 (7)	0.6694 (3)	0.0289 (4)
H9	0.724466	0.267531	0.717834	0.035*
C10	0.9098 (3)	0.21487 (7)	0.6967 (3)	0.0274 (4)
C11	0.9208 (3)	0.16984 (7)	0.6270 (3)	0.0257 (4)
H11	1.050455	0.156221	0.646503	0.031*
C12	0.7369 (3)	0.14524 (6)	0.5279 (3)	0.0206 (3)
H12	0.740333	0.114189	0.478782	0.025*
C13	0.3950 (3)	0.11531 (6)	0.0192 (2)	0.0190 (3)
C14	0.4165 (3)	0.03381 (7)	0.1955 (3)	0.0259 (4)
C15	0.0753 (3)	0.05941 (6)	-0.1081 (3)	0.0207 (4)

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cr1	0.02042 (17)	0.01303 (16)	0.01223 (16)	-0.00087 (9)	0.00954 (12)	-0.00134 (9)
F1	0.0372 (7)	0.0362 (7)	0.0445 (7)	-0.0186 (6)	-0.0026 (6)	0.0048 (6)
O1	0.0274 (7)	0.0454 (8)	0.0234 (7)	-0.0098 (6)	0.0153 (6)	0.0014 (6)

O2	0.0717 (11)	0.0378 (8)	0.0347 (8)	0.0311 (8)	0.0301 (8)	0.0127 (6)
O3	0.0417 (8)	0.0275 (7)	0.0212 (7)	−0.0131 (6)	0.0116 (6)	−0.0081 (5)
C1	0.0234 (8)	0.0145 (7)	0.0140 (7)	0.0003 (6)	0.0118 (7)	−0.0032 (6)
C2	0.0304 (9)	0.0169 (8)	0.0135 (8)	−0.0011 (7)	0.0127 (7)	−0.0013 (6)
C3	0.0379 (10)	0.0199 (8)	0.0216 (8)	−0.0069 (7)	0.0223 (8)	−0.0047 (7)
C4	0.0279 (10)	0.0282 (9)	0.0276 (10)	−0.0094 (7)	0.0201 (8)	−0.0095 (7)
C5	0.0206 (8)	0.0265 (9)	0.0233 (9)	0.0010 (7)	0.0129 (7)	−0.0055 (7)
C6	0.0233 (8)	0.0152 (7)	0.0204 (8)	0.0028 (6)	0.0135 (7)	−0.0023 (6)
C7	0.0242 (8)	0.0143 (7)	0.0117 (7)	−0.0008 (6)	0.0082 (6)	0.0000 (6)
C8	0.0289 (9)	0.0168 (8)	0.0206 (8)	0.0013 (7)	0.0082 (7)	−0.0027 (7)
C9	0.0412 (11)	0.0161 (8)	0.0244 (9)	−0.0054 (7)	0.0086 (8)	−0.0022 (7)
C10	0.0281 (10)	0.0262 (9)	0.0190 (9)	−0.0108 (8)	0.0006 (7)	0.0048 (7)
C11	0.0237 (9)	0.0285 (9)	0.0216 (9)	0.0002 (7)	0.0061 (7)	0.0066 (7)
C12	0.0260 (9)	0.0181 (8)	0.0179 (8)	0.0018 (7)	0.0091 (7)	0.0006 (6)
C13	0.0187 (8)	0.0240 (8)	0.0136 (7)	−0.0004 (7)	0.0058 (6)	−0.0036 (6)
C14	0.0420 (11)	0.0239 (9)	0.0164 (8)	0.0075 (8)	0.0165 (8)	0.0030 (7)
C15	0.0291 (9)	0.0158 (8)	0.0217 (9)	−0.0041 (7)	0.0150 (7)	−0.0004 (7)

Geometric parameters (Å, °)

Cr1—C1	2.2316 (15)	C3—H3	0.9500
Cr1—C2	2.2061 (17)	C3—C4	1.395 (3)
Cr1—C3	2.2118 (16)	C4—H4	0.9500
Cr1—C4	2.2104 (18)	C4—C5	1.417 (3)
Cr1—C5	2.2160 (17)	C5—H5	0.9500
Cr1—C6	2.2102 (16)	C5—C6	1.405 (2)
Cr1—C13	1.8417 (17)	C6—H6	0.9500
Cr1—C14	1.8432 (19)	C7—C8	1.399 (2)
Cr1—C15	1.8448 (18)	C7—C12	1.391 (2)
F1—C10	1.355 (2)	C8—H8	0.9500
O1—C13	1.152 (2)	C8—C9	1.389 (3)
O2—C14	1.154 (2)	C9—H9	0.9500
O3—C15	1.151 (2)	C9—C10	1.373 (3)
C1—C2	1.410 (2)	C10—C11	1.382 (3)
C1—C6	1.422 (2)	C11—H11	0.9500
C1—C7	1.485 (2)	C11—C12	1.383 (3)
C2—H2	0.9500	C12—H12	0.9500
C2—C3	1.417 (3)		
C2—Cr1—C1	37.05 (6)	C3—C2—H2	119.6
C2—Cr1—C3	37.42 (7)	Cr1—C3—H3	129.8
C2—Cr1—C4	66.90 (7)	C2—C3—Cr1	71.07 (9)
C2—Cr1—C5	79.11 (7)	C2—C3—H3	120.1
C2—Cr1—C6	66.85 (6)	C4—C3—Cr1	71.55 (10)
C3—Cr1—C1	67.19 (6)	C4—C3—C2	119.89 (16)
C3—Cr1—C5	66.85 (7)	C4—C3—H3	120.1
C4—Cr1—C1	79.33 (6)	Cr1—C4—H4	129.3
C4—Cr1—C3	36.79 (8)	C3—C4—Cr1	71.66 (10)

C4—Cr1—C5	37.34 (7)	C3—C4—H4	119.9
C5—Cr1—C1	67.15 (6)	C3—C4—C5	120.29 (17)
C6—Cr1—C1	37.33 (6)	C5—C4—Cr1	71.55 (10)
C6—Cr1—C3	79.03 (6)	C5—C4—H4	119.9
C6—Cr1—C4	66.95 (6)	Cr1—C5—H5	129.8
C6—Cr1—C5	37.01 (6)	C4—C5—Cr1	71.12 (10)
C13—Cr1—C1	91.52 (7)	C4—C5—H5	120.2
C13—Cr1—C2	120.24 (7)	C6—C5—Cr1	71.27 (9)
C13—Cr1—C3	157.48 (7)	C6—C5—C4	119.56 (17)
C13—Cr1—C4	149.93 (7)	C6—C5—H5	120.2
C13—Cr1—C5	112.78 (7)	Cr1—C6—H6	129.0
C13—Cr1—C6	88.41 (7)	C1—C6—Cr1	72.15 (9)
C13—Cr1—C14	89.70 (8)	C1—C6—H6	119.5
C13—Cr1—C15	89.56 (7)	C5—C6—Cr1	71.72 (10)
C14—Cr1—C1	113.21 (7)	C5—C6—C1	120.98 (15)
C14—Cr1—C2	88.90 (7)	C5—C6—H6	119.5
C14—Cr1—C3	92.09 (7)	C8—C7—C1	119.86 (15)
C14—Cr1—C4	120.27 (8)	C12—C7—C1	120.85 (14)
C14—Cr1—C5	157.49 (8)	C12—C7—C8	119.22 (16)
C14—Cr1—C6	150.36 (8)	C7—C8—H8	119.8
C14—Cr1—C15	88.88 (8)	C9—C8—C7	120.42 (17)
C15—Cr1—C1	157.89 (7)	C9—C8—H8	119.8
C15—Cr1—C2	150.09 (7)	C8—C9—H9	120.9
C15—Cr1—C3	112.91 (7)	C10—C9—C8	118.24 (17)
C15—Cr1—C4	88.78 (7)	C10—C9—H9	120.9
C15—Cr1—C5	92.13 (7)	F1—C10—C9	118.94 (18)
C15—Cr1—C6	120.68 (7)	F1—C10—C11	117.83 (18)
C2—C1—Cr1	70.49 (9)	C9—C10—C11	123.23 (17)
C2—C1—C6	118.43 (15)	C10—C11—H11	121.1
C2—C1—C7	120.19 (15)	C10—C11—C12	117.86 (17)
C6—C1—Cr1	70.52 (9)	C12—C11—H11	121.1
C6—C1—C7	121.38 (14)	C7—C12—H12	119.5
C7—C1—Cr1	130.85 (11)	C11—C12—C7	121.02 (16)
Cr1—C2—H2	128.8	C11—C12—H12	119.5
C1—C2—Cr1	72.46 (9)	O1—C13—Cr1	178.29 (16)
C1—C2—H2	119.6	O2—C14—Cr1	179.2 (2)
C1—C2—C3	120.84 (16)	O3—C15—Cr1	179.48 (18)
C3—C2—Cr1	71.51 (10)		
Cr1—C1—C2—C3	−54.82 (14)	C3—C4—C5—Cr1	54.62 (15)
Cr1—C1—C6—C5	54.72 (14)	C3—C4—C5—C6	0.4 (2)
Cr1—C1—C7—C8	144.23 (14)	C4—C5—C6—Cr1	54.18 (14)
Cr1—C1—C7—C12	−38.8 (2)	C4—C5—C6—C1	−0.7 (2)
Cr1—C2—C3—C4	−54.34 (14)	C6—C1—C2—Cr1	53.55 (13)
Cr1—C3—C4—C5	−54.56 (15)	C6—C1—C2—C3	−1.3 (2)
Cr1—C4—C5—C6	−54.26 (14)	C6—C1—C7—C8	53.6 (2)
Cr1—C5—C6—C1	−54.92 (13)	C6—C1—C7—C12	−129.43 (17)
F1—C10—C11—C12	178.40 (16)	C7—C1—C2—Cr1	−126.63 (14)

C1—C2—C3—Cr1	55.26 (14)	C7—C1—C2—C3	178.55 (14)
C1—C2—C3—C4	0.9 (2)	C7—C1—C6—Cr1	126.65 (14)
C1—C7—C8—C9	175.90 (16)	C7—C1—C6—C5	−178.63 (14)
C1—C7—C12—C11	−176.06 (15)	C7—C8—C9—C10	0.3 (3)
C2—C1—C6—Cr1	−53.54 (13)	C8—C7—C12—C11	0.9 (2)
C2—C1—C6—C5	1.2 (2)	C8—C9—C10—F1	−178.58 (17)
C2—C1—C7—C8	−126.21 (17)	C8—C9—C10—C11	0.9 (3)
C2—C1—C7—C12	50.8 (2)	C9—C10—C11—C12	−1.1 (3)
C2—C3—C4—Cr1	54.12 (14)	C10—C11—C12—C7	0.1 (3)
C2—C3—C4—C5	−0.4 (3)	C12—C7—C8—C9	−1.1 (3)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C6—H6···F1 ⁱ	0.95	2.48	3.122 (2)	125
C8—H8···F1 ⁱ	0.95	2.46	3.295 (2)	147

Symmetry code: (i) $x-1, -y+1/2, z-1/2$.**4-Fluoro-1,1'-biphenyl (czerwinski13)***Crystal data*C₁₂H₉F $M_r = 172.19$ Orthorhombic, *Fdd2* $a = 12.9824$ (9) Å $b = 23.0588$ (15) Å $c = 5.7527$ (4) Å $V = 1722.1$ (2) Å³ $Z = 8$ $F(000) = 720$ *Data collection*

Bruker SMART APEXII

diffractometer

Radiation source: sealed X-ray tube, Siemens, K

FFCU 2K 90

Equatorially mounted graphite monochromator

Detector resolution: 7.9 pixels mm^{−1}0.60° ω and 0.6° ϕ scans

Absorption correction: multi-scan

(SADABS; Krause *et al.*, 2015)*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.039$ $wR(F^2) = 0.107$ $S = 1.13$

836 reflections

64 parameters

1 restraint

Primary atom site location: dual

 $D_x = 1.328$ Mg m^{−3}Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 5876 reflections

 $\theta = 7.7$ – 72.8° $\mu = 0.74$ mm^{−1} $T = 100$ K

Needle, colourless

0.56 × 0.14 × 0.02 mm

 $T_{\min} = 0.671, T_{\max} = 0.754$

7085 measured reflections

836 independent reflections

825 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.028$ $\theta_{\max} = 72.8^\circ, \theta_{\min} = 7.7^\circ$ $h = -15 \rightarrow 15$ $k = -28 \rightarrow 28$ $l = -7 \rightarrow 7$ Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0611P)^2 + 2.1311P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.36$ e Å^{−3} $\Delta\rho_{\min} = -0.16$ e Å^{−3}

Absolute structure: Flack x determined using
 351 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
 Absolute structure parameter: -0.07 (17)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
F1	0.5021 (2)	0.56162 (12)	0.7706 (5)	0.0335 (8)	0.5
C1	0.54787 (16)	0.51796 (9)	0.4167 (4)	0.0223 (6)	
C2	0.57037 (17)	0.55520 (10)	0.6000 (4)	0.0244 (6)	0.5
H2	0.524692	0.556868	0.728848	0.029*	
C3	0.65725 (19)	0.58986 (10)	0.6001 (5)	0.0277 (6)	
H3	0.670501	0.615208	0.726828	0.033*	
C4	0.72528 (19)	0.58731 (10)	0.4129 (4)	0.0280 (6)	
H4	0.784987	0.611122	0.410672	0.034*	
C5	0.70540 (18)	0.54998 (10)	0.2306 (5)	0.0277 (6)	
H5	0.752322	0.547626	0.104202	0.033*	
C6	0.61707 (18)	0.51579 (10)	0.2308 (4)	0.0247 (6)	
H6	0.603680	0.490710	0.103350	0.030*	

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0373 (16)	0.0363 (15)	0.0268 (16)	-0.0006 (12)	0.0046 (12)	-0.0015 (13)
C1	0.0202 (10)	0.0220 (11)	0.0247 (14)	0.0034 (9)	-0.0026 (9)	0.0043 (9)
C2	0.0245 (11)	0.0258 (12)	0.0228 (14)	0.0037 (9)	0.0003 (10)	0.0001 (10)
C3	0.0301 (13)	0.0259 (11)	0.0272 (13)	-0.0006 (9)	-0.0054 (11)	0.0003 (10)
C4	0.0228 (11)	0.0272 (11)	0.0340 (14)	-0.0019 (9)	-0.0032 (10)	0.0047 (11)
C5	0.0227 (11)	0.0327 (12)	0.0278 (13)	0.0019 (9)	0.0015 (10)	0.0056 (11)
C6	0.0247 (11)	0.0264 (11)	0.0229 (12)	0.0027 (9)	0.0001 (10)	-0.0007 (9)

Geometric parameters ($\text{\AA}$, $^\circ$)

F1—C2	1.331 (4)	C3—C4	1.394 (4)
C1—C1 ⁱ	1.494 (4)	C4—H4	0.9500
C1—C2	1.391 (3)	C4—C5	1.381 (4)
C1—C6	1.397 (3)	C5—H5	0.9500
C2—H2	0.9500	C5—C6	1.392 (4)
C2—C3	1.382 (3)	C6—H6	0.9500
C3—H3	0.9500		
C2—C1—C1 ⁱ	121.13 (16)	C4—C3—H3	120.3

C2—C1—C6	117.9 (2)	C3—C4—H4	120.2
C6—C1—C1 ⁱ	121.01 (17)	C5—C4—C3	119.6 (2)
F1—C2—C1	119.2 (2)	C5—C4—H4	120.2
F1—C2—C3	118.6 (2)	C4—C5—H5	119.8
C1—C2—H2	119.0	C4—C5—C6	120.4 (2)
C3—C2—C1	121.9 (2)	C6—C5—H5	119.8
C3—C2—H2	119.0	C1—C6—H6	119.7
C2—C3—H3	120.3	C5—C6—C1	120.7 (2)
C2—C3—C4	119.5 (2)	C5—C6—H6	119.7
F1—C2—C3—C4	−174.6 (2)	C2—C3—C4—C5	−0.4 (3)
C1 ⁱ —C1—C2—F1	−4.4 (4)	C3—C4—C5—C6	1.2 (4)
C1 ⁱ —C1—C2—C3	−178.3 (2)	C4—C5—C6—C1	−1.0 (4)
C1 ⁱ —C1—C6—C5	179.1 (2)	C6—C1—C2—F1	174.8 (2)
C1—C2—C3—C4	−0.6 (3)	C6—C1—C2—C3	0.9 (3)
C2—C1—C6—C5	−0.1 (3)		

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

2-Fluoro-1,1'-biphenyl (czerwinski12)

Crystal data

C₁₂H₉F

$M_r = 172.19$

Orthorhombic, *Pbcn*

$a = 5.6462$ (14) Å

$b = 20.739$ (5) Å

$c = 7.292$ (2) Å

$V = 853.9$ (4) Å³

$Z = 4$

$F(000) = 360$

Data collection

Bruker APEXII Quazar
diffractometer

Radiation source: microfocus sealed X-ray tube,
Incoatec I μ s

Mirror optics monochromator

Detector resolution: 7.9 pixels mm^{−1}

0.5° ω and 0.5° φ scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$D_x = 1.339$ Mg m^{−3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 6339 reflections

$\theta = 3.4$ – 28.3°

$\mu = 0.09$ mm^{−1}

$T = 100$ K

Needle, colourless

0.39 × 0.11 × 0.03 mm

$T_{\min} = 0.706$, $T_{\max} = 0.746$

19177 measured reflections

1055 independent reflections

899 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 2.0^\circ$

$h = -7 \rightarrow 7$

$k = -27 \rightarrow 27$

$l = -9 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.143$

$S = 1.11$

1055 reflections

68 parameters

1 restraint

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0828P)^2 + 0.1921P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.45$ e Å^{−3}

$\Delta\rho_{\min} = -0.16$ e Å^{−3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
F1	0.500000	0.95466 (5)	0.250000	0.0291 (4)	0.789 (2)
F2	0.500000	0.48895 (18)	0.250000	0.0321 (12)	0.211 (2)
C1	0.500000	0.89062 (7)	0.250000	0.0218 (3)	
H1	0.499999	0.936429	0.249997	0.026*	0.211 (2)
C2	0.31493 (18)	0.85859 (5)	0.33221 (14)	0.0241 (3)	
H2	0.189391	0.881754	0.388628	0.029*	
C3	0.31572 (17)	0.79142 (5)	0.33088 (13)	0.0217 (3)	
H3	0.187996	0.768828	0.386240	0.026*	
C4	0.500000	0.75641 (6)	0.250000	0.0161 (3)	
C5	0.500000	0.68428 (7)	0.250000	0.0166 (3)	
C6	0.31769 (18)	0.64928 (5)	0.33289 (14)	0.0247 (3)	
H6	0.191342	0.671769	0.390424	0.030*	
C7	0.3172 (2)	0.58230 (6)	0.33300 (15)	0.0280 (3)	
H7	0.191316	0.559467	0.390068	0.034*	
C8	0.500000	0.54887 (7)	0.250000	0.0258 (4)	
H8	0.499999	0.503065	0.250001	0.031*	0.789 (2)

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0344 (7)	0.0153 (6)	0.0376 (7)	0.000	0.0039 (5)	0.000
F2	0.039 (2)	0.0129 (19)	0.045 (3)	0.000	0.006 (2)	0.000
C1	0.0233 (7)	0.0219 (7)	0.0200 (7)	0.000	−0.0026 (5)	0.000
C2	0.0215 (6)	0.0255 (6)	0.0253 (5)	0.0067 (4)	0.0048 (4)	0.0030 (4)
C3	0.0174 (5)	0.0247 (6)	0.0229 (5)	0.0024 (4)	0.0050 (4)	0.0056 (4)
C4	0.0140 (6)	0.0221 (7)	0.0122 (6)	0.000	−0.0016 (4)	0.000
C5	0.0147 (6)	0.0221 (7)	0.0131 (6)	0.000	−0.0012 (5)	0.000
C6	0.0213 (5)	0.0245 (6)	0.0281 (6)	−0.0038 (4)	0.0075 (4)	−0.0067 (4)
C7	0.0269 (6)	0.0252 (6)	0.0319 (6)	−0.0085 (4)	0.0078 (4)	−0.0044 (4)
C8	0.0296 (8)	0.0218 (7)	0.0259 (7)	0.000	−0.0002 (6)	0.000

Geometric parameters ($\text{\AA}$, $^\circ$)

F1—C1	1.3280 (17)	C4—C5	1.4959 (19)
F2—C8	1.243 (4)	C5—C6	1.3971 (12)
C1—H1	0.9500	C5—C6 ⁱ	1.3972 (12)
C1—C2	1.3758 (13)	C6—H6	0.9500
C1—C2 ⁱ	1.3758 (13)	C6—C7	1.3891 (16)
C2—H2	0.9500	C7—H7	0.9500

C2—C3	1.3931 (15)	C7—C8	1.3829 (13)
C3—H3	0.9500	C8—H8	0.9500
C3—C4	1.3991 (12)		
F1—C1—C2	118.88 (7)	C6 ⁱ —C5—C4	121.31 (7)
F1—C1—C2 ⁱ	118.88 (7)	C6—C5—C4	121.31 (7)
C2 ⁱ —C1—H1	118.9	C6—C5—C6 ⁱ	117.39 (13)
C2—C1—H1	118.9	C5—C6—H6	119.3
C2—C1—C2 ⁱ	122.25 (14)	C7—C6—C5	121.42 (10)
C1—C2—H2	120.7	C7—C6—H6	119.3
C1—C2—C3	118.52 (10)	C6—C7—H7	120.0
C3—C2—H2	120.7	C8—C7—C6	119.97 (10)
C2—C3—H3	119.2	C8—C7—H7	120.0
C2—C3—C4	121.62 (9)	F2—C8—C7 ⁱ	120.09 (7)
C4—C3—H3	119.2	F2—C8—C7	120.09 (7)
C3 ⁱ —C4—C3	117.48 (13)	C7 ⁱ —C8—C7	119.83 (14)
C3 ⁱ —C4—C5	121.26 (7)	C7—C8—H8	120.1
C3—C4—C5	121.26 (7)	C7 ⁱ —C8—H8	120.1
F1—C1—C2—C3	179.71 (6)	C3 ⁱ —C4—C5—C6	179.12 (7)
C1—C2—C3—C4	0.59 (13)	C3—C4—C5—C6	−0.88 (7)
C2 ⁱ —C1—C2—C3	−0.29 (6)	C4—C5—C6—C7	179.96 (7)
C2—C3—C4—C3 ⁱ	−0.30 (7)	C5—C6—C7—C8	0.07 (14)
C2—C3—C4—C5	179.70 (7)	C6 ⁱ —C5—C6—C7	−0.04 (7)
C3 ⁱ —C4—C5—C6 ⁱ	−0.88 (7)	C6—C7—C8—F2	179.96 (7)
C3—C4—C5—C6 ⁱ	179.12 (7)	C6—C7—C8—C7 ⁱ	−0.04 (7)

Symmetry code: (i) $-x+1, y, -z+1/2$.