Electronic Supplementary Information

Organometallic Halogen Bond Acceptors: Directionality, Hybrid Cocrystals Precipitation and a Blueshift of CO Ligand Vibrational Band.

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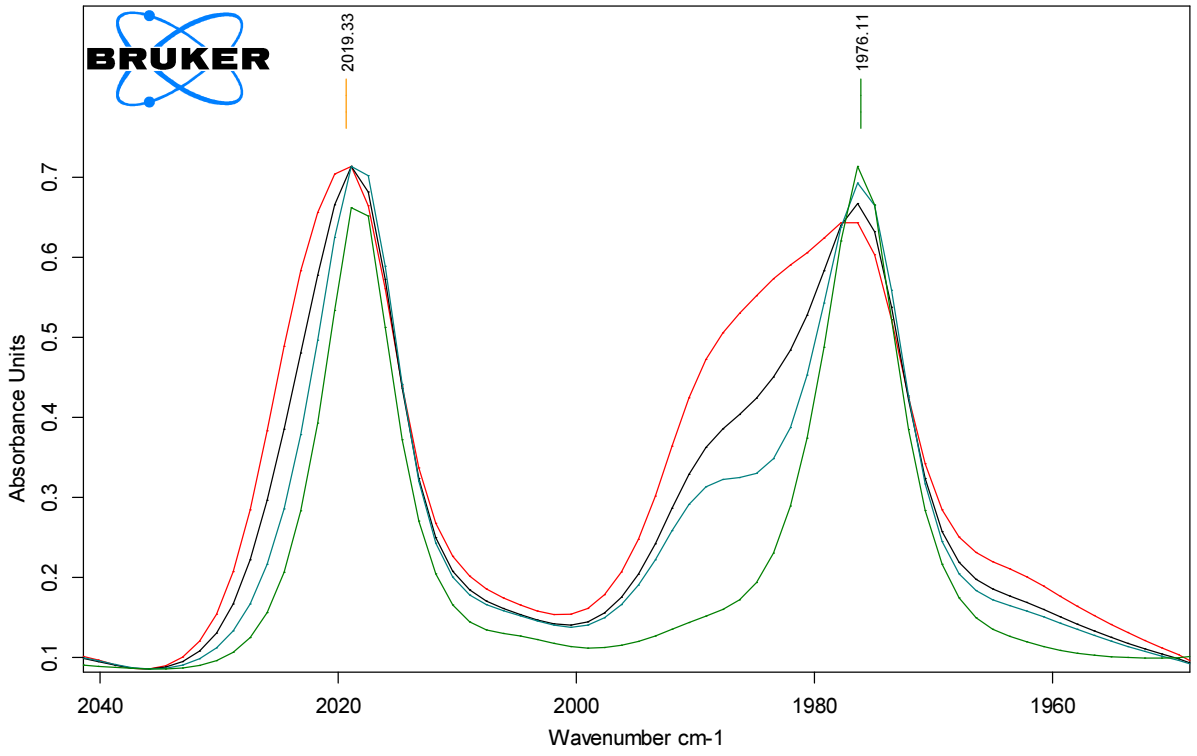


Figure 1_es. Unsymmetrical hypsochromic broadening (by ~4 cm^{-1} half-width) of the CO band at 2019 cm^{-1} in $CpFe(CO)_2TePh$ titrated in cyclohexane against *p*-DITFB.

Table 1_es Line charecteristics for the Figure 1_es

Line	Maximum cm^{-1}	Full width (at half maximum), cm^{-1}
1	2018.49	7.88
2	2018.32	8.99
3	2018.70	10.68
4	2019.33	12.38

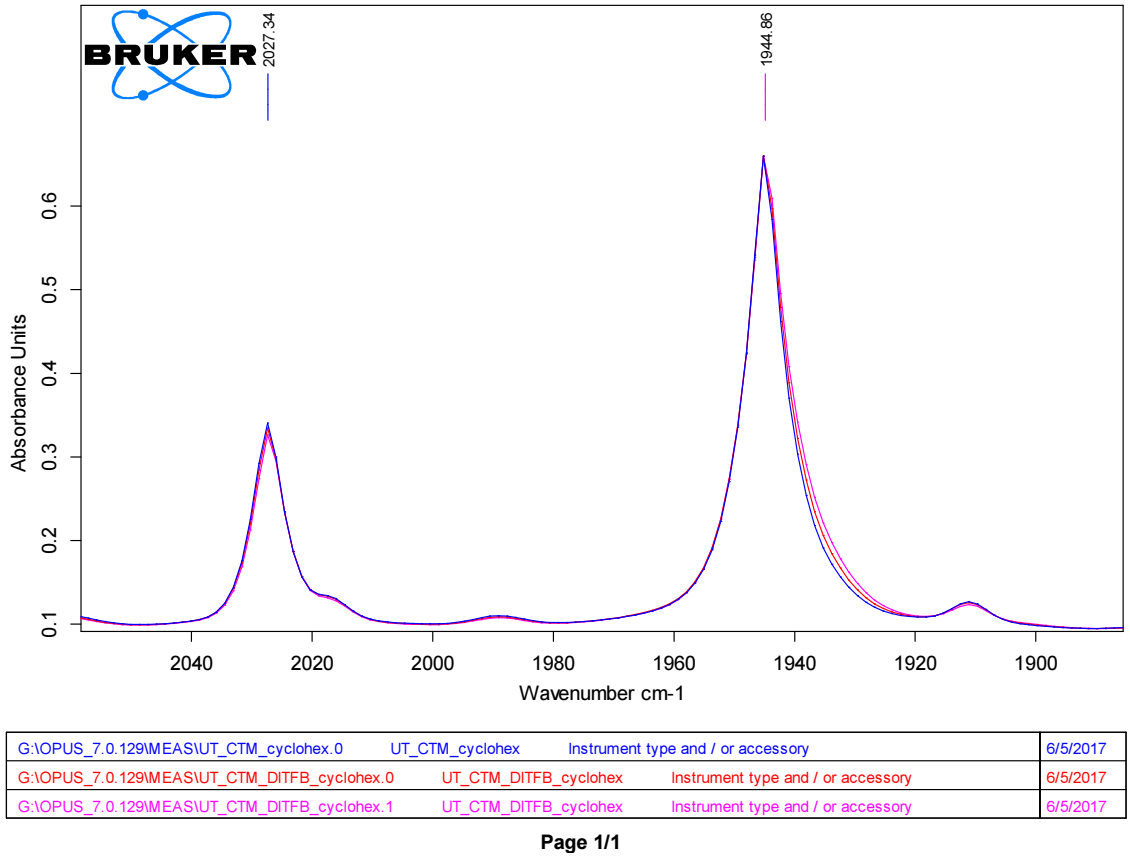


Figure 2_es. Unsymmetrical bathochromic broadening of the CO band at 1945 cm^{-1} in $CpMn(CO)_3$ titrated in cyclohexane against *p*-DITFB

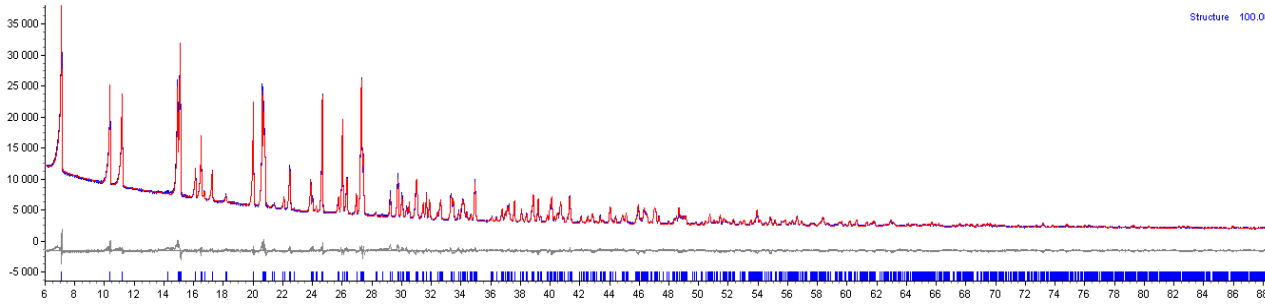


Figure 3_es.

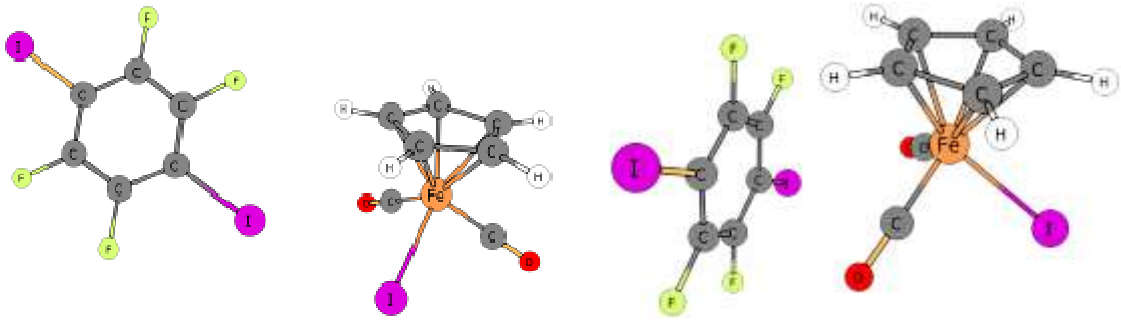
Modeling of the diffractogram of a $CpFe(CO)_2TePh$ / *p*-DITFB sample by the Rietveld method: Experimental (blue, for fine powder precipitated upon the mixing $CpFe(CO)_2TePh$ solution in hexane with *p*-DITFB) .calculated (red, from the single crystal XRD data for $CpFe(CO)_2TePh$ / *p*-DITFB cocrystals) and differential (gray) curves.

Computations

	Free complex	DITFB adduct, (experiment)	shift cm^{-1}	Free complex	DITFB adduct (calculated)	shift cm^{-1}

	(experiment) ν, cm^{-1}	ν, cm^{-1}		(calculated) ν, cm^{-1}	I----X I----π-CO ν, cm^{-1}	
$CpFe(CO)_2Cl$	2048, 1990	2048, **2003**	0, 13	2044, 2003	2047, 2007 2038, 1994	3, 3 -6, -9
$CpFe(CO)_2I$	2026, **1966, 1946**	2032**, 1982, 1962**	6, 16, 16	2034, 1997	2038, 2000 2028, 1986	4, 3 -6, -9
$CpFe(CO)_2TePh$	2007, 1993, 1936	2013, 1993, 1941 [a]	6, 0, 5	2013, 1976	2020, 1983 2007, 1965	7, 7 -6, -9

Table 1_es. Calculated and experimental (FTIR-ATR) CO frequencies for pure $CpFe(CO)_2X$ and its adducts with *p*-DITFB.



a **b**

Figure 4_es. Calculated geometry of $CpFe(CO)_2I$(DITFB) adducts associated trough the I---I (**a**) and I----π(CO) (**b**) halogen bonds

	PBE0-D3 def-2TZVP	DLPNO-CCSD(T) def2-TZVP	DLPNO-CCSD(T) def2-CBS(2/3)	DLPNO-CCSD(T) def2-QZVP	DLPNO-CCSD(T) def2-CBS(3/4)	ZPE+thermal correction to ΔH
$CpFe(CO)_2Cl$ (X-I)	-8.54	-7.87	-9.65	-8.30	-8.57	1.76
$CpFe(CO)_2Cl$ (π-CO)	-6.74	-7.87	-9.24	-7.20	-7.02	1.83
$CpFe(CO)_2I$ (X-I)	-8.01	-6.73	-8.45	-7.34	-7.64	1.75
$CpFe(CO)_2I$ (π-CO)	-6.85	-7.67	-8.85	-7.49	-7.52	1.22
$CpFe(CO)_2TePh$ (X-I)	-13.77	-9.92	-12.42	-10.66	-10.97	1.33
$CpFe(CO)_2TePh$ (π-CO)	-11.64	-11.61	-13.90	-11.93	-12.16	0.88

Table 2_es. Energies of I---X and I----π-CO halogen-bond complexes formation with DITFB from single point calculation on PBE/def2-TZVP geometries.

Second order perturbation theory analysis of Fock matrix in NBO basis for $CpFe(CO)_2X$→DITFB donor-acceptor interaction.

X=Cl

LP(Cl $sp^{0.44}$)→ σ^*(C $sp^{2.66}$-I $sp^{13.02}$)	0.78
LP(Cl $sp^{11.71}$)→ σ^*(C -I)	0.12
LP(Cl $sp^{11.71}$)→ RY(I)	0.05
LP(Cl $sp^{10.52}$)→ σ^*(C -I)	**9.23**
LP(Cl $sp^{10.52}$)→ RY(I)	0.71 (sum of)
σ(Fe $sd^{2.38}$– Cl $sp^{6.21}$) → σ^*(C -I)	0.08
σ (Fe $sd^{1.85}$– C_{CO} $sp^{0.51}$) → σ^*(C -I)	0.09

X=I

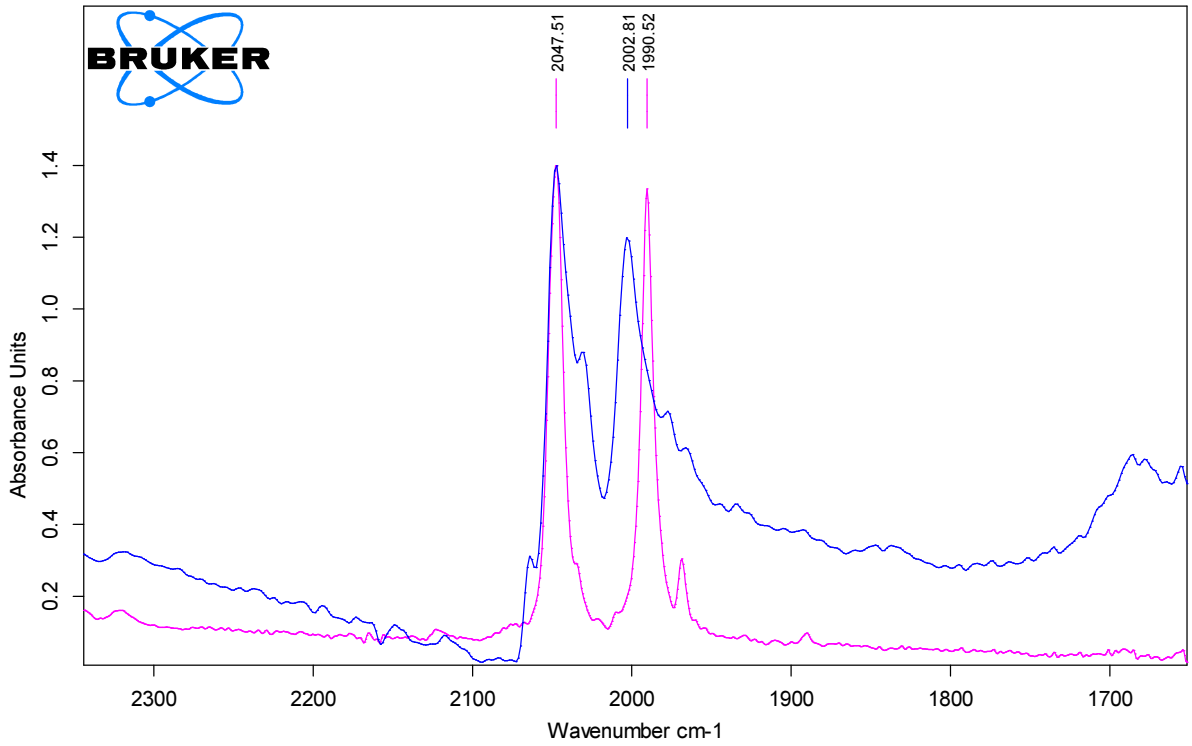
LP(I $sp^{0.21}$) → σ^*(C $sp^{2.69}$-I $sp^{13.24}$)	0.74
LP(I $sp^{26.36}$) → σ^*(C - I)	0.05
LP(I $sp^{26.36}$) → RY(I)	0.08
LP(I $sp^{21.54}$) → σ^*(C - I)	**10.56**
LP(I $sp^{21.54}$) → RY(I)	1.21
σ (Fe $sd^{2.5}$– I $sp^{10.07}$) →σ^*(C - I)	0.10

X=TePh

LP (Te $sp^{0.31}$) → σ^*(C $sp^{2.73}$-I $sp^{18.45}$)	1.52
LP (Te $sp^{15.03}$) → σ^*(C-I)	**22.81**
LP (Te $sp^{15.03}$) → RY(I)	3.92 (sum of many Rydberg orbitals)
σ (Fe sd^3 – Te $sp^{12.5}$) → σ^*(C-I)	0.05
σ (C $sp^{2.56}$- H s) → σ^*(C-I)	0.13

The same computational method that we use for our complexes (although, not perfectly exact about the absolute νCO values) correctly reproduces the 7 cm^{-1} shift observed in [] for $[(Me_5C_5)Fe(CO)_2I]_2$--I_2 complex.
Calculated ν, cm^{-1} CO for Cp"$Fe(CO)_2I$ 2014, 1976
Calculated ν, cm^{-1} CO for Cp"$Fe(CO)_2$ -I_2 2023, 1985

ATR-FTIR spaectra for complexes 3-6



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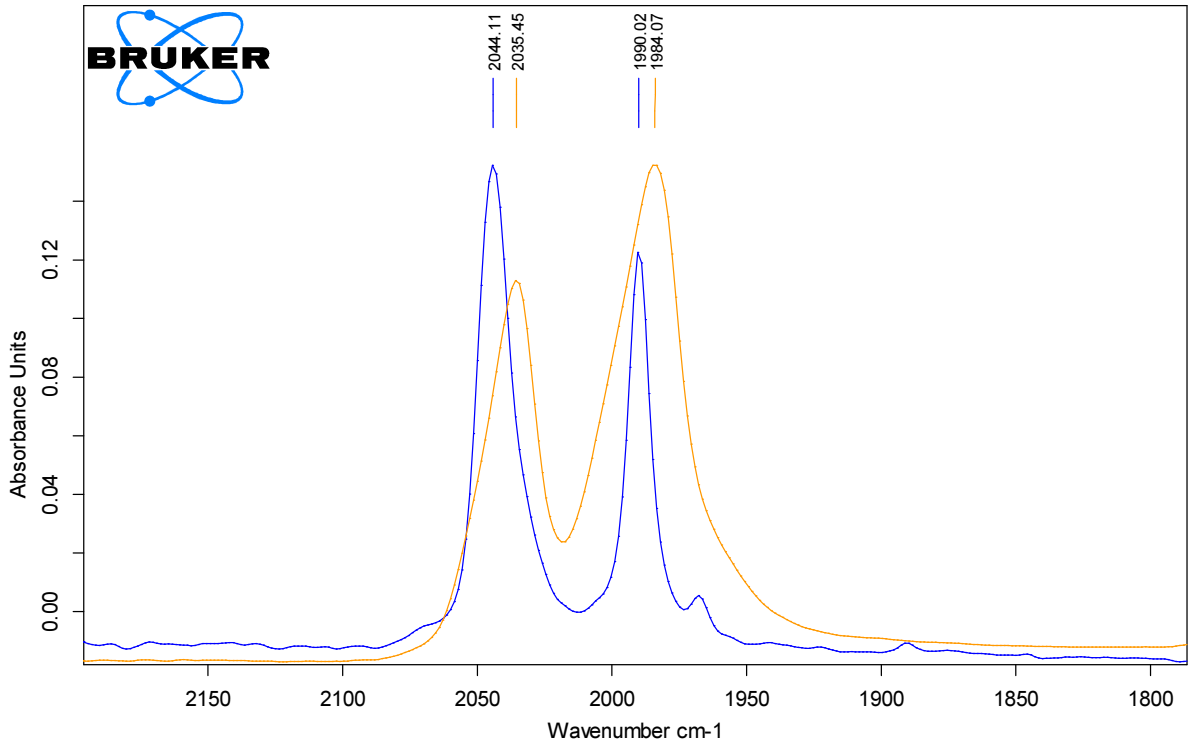
IR spectra for $CpFe(CO)_2Cl$ and $[CpFe(CO)_2Cl][\mu$-*p*- DITFB] (complex **3**)



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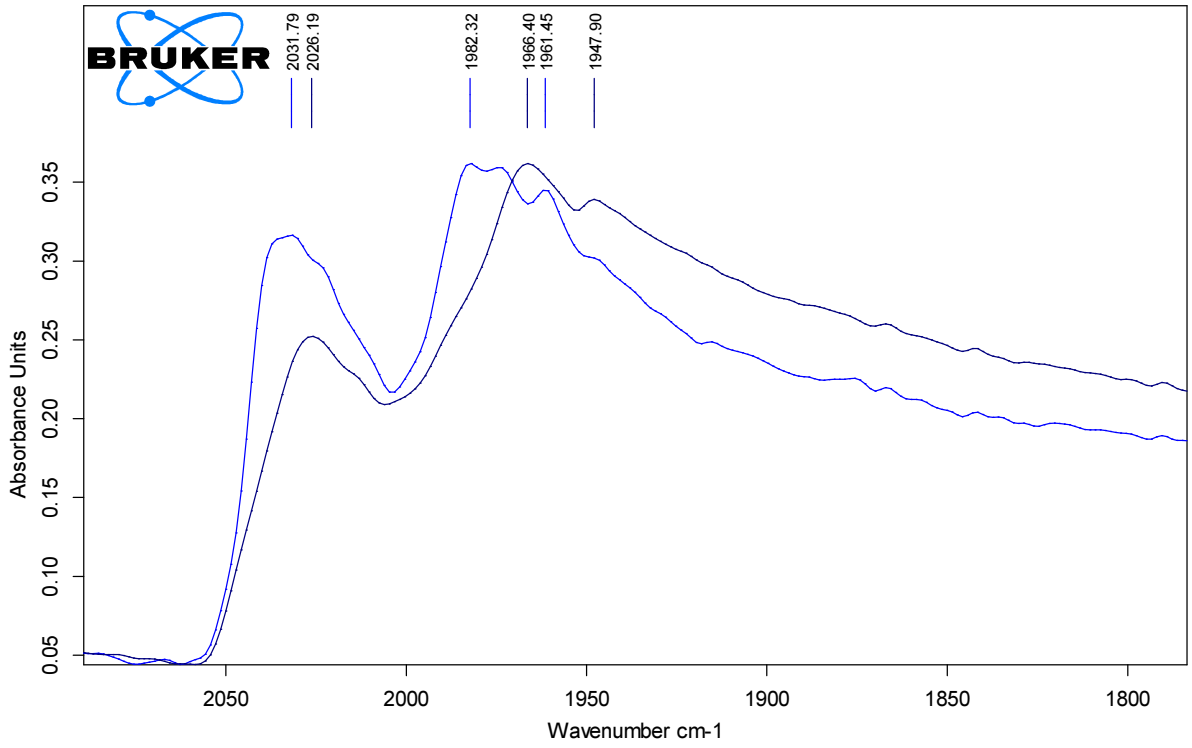
IR spectra for $CpFe(CO)_2Br$ and $[CpFe(CO)_2Br][\mu$-*p*- DITFB] (complex **4**)



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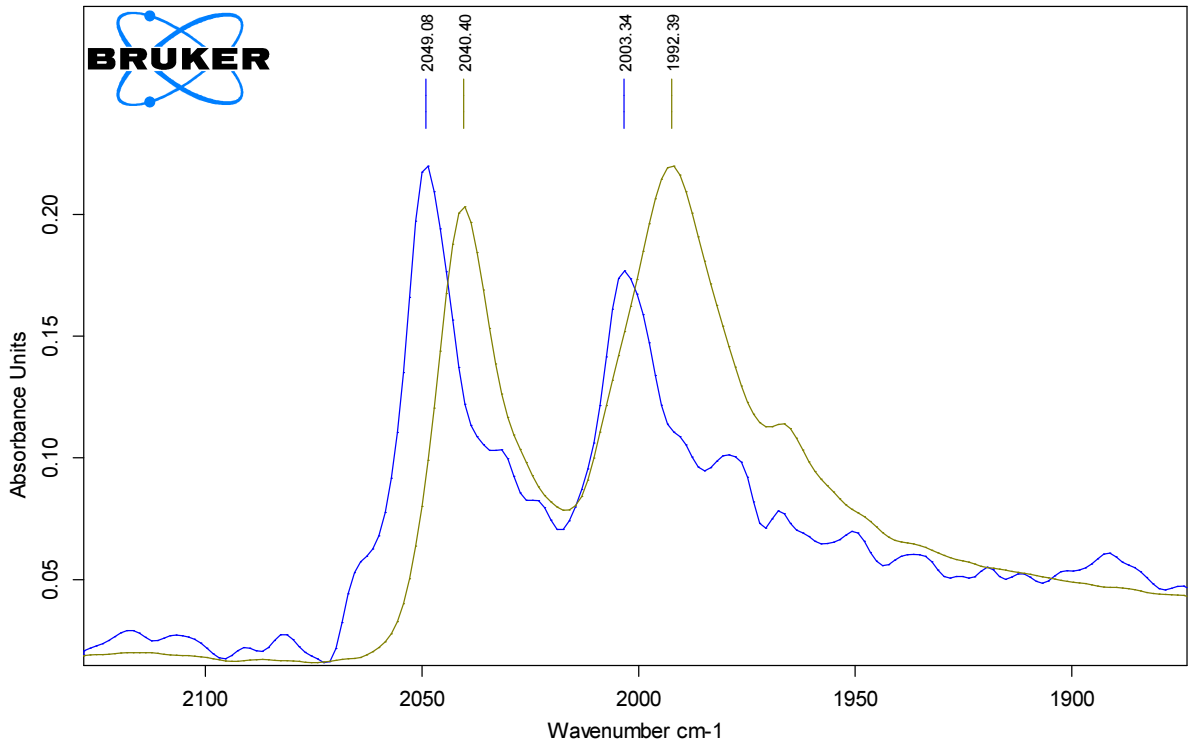
IR spectra for $CpFe(CO)_2I$ and $[CpFe(CO)_2I][\mu$-*p*- DITFB] (complex **5**)



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IR spectra for $CbCo(CO)_2I$ and $[CbCo(CO)_2I]$ [μ-*p*- DITFB] (complex **6**)

Crystallographic data for complexes 1-7

Complex 1.1 $CpFe(CO)_2TePh$----*p*-DITFB

Table 3 Crystal data and structure refinement for 1__CpFe-TePh-DITFB.

Identification code	1__CpFe-TePh-DITFB
Empirical formula	$C_{16}H_{10}F_2FeIO_2Te$
Formula weight	582.59
Temperature/K	423(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.5280(4)
b/Å	11.6432(4)
c/Å	11.7133(4)
α/°	90
β/°	114.97
γ/°	90
Volume/$Å^3$	1672.45(9)
Z	4
$\rho_{calc}g/cm^3$	2.314
μ/mm^{-1}	4.482
F(000)	1084.0
Crystal size/mm^3	0.400 × 0.300 × 0.200
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.824 to 56.802
Index ranges	$-18 \le h \le 18$, $-15 \le k \le 15$, $-15 \le l \le 15$
Reflections collected	17477
Independent reflections	4178 [R_{int} = 0.0243, R_{sigma} = 0.0200]
Data/restraints/parameters	4178/0/208
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0183, wR_2 = 0.0409
Final R indexes [all data]	R_1 = 0.0212, wR_2 = 0.0420
Largest diff. peak/hole / e $Å^{-3}$	0.65/-0.55

Table 3.1 Bond Lengths for 1__CpFe-TePh-DITFB.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Te(1)	C(8)	2.130(2)	C(13)	C(12)	1.388(3)
Te(1)	Fe(1)	2.5934(3)	C(13)	C(8)	1.391(3)
I(1)	C(14)	2.111(2)	C(8)	C(9)	1.393(3)
Fe(1)	C(1)	1.760(2)	C(19)	$C(15)^1$	1.379(3)
Fe(1)	C(2)	1.770(2)	C(19)	C(14)	1.380(3)
Fe(1)	C(7)	2.088(2)	C(14)	C(15)	1.383(3)
Fe(1)	C(3)	2.089(2)	C(9)	C(10)	1.395(3)

Fe(1)	C(4)	2.103(2)	C(12)	C(11)	1.379(3)
Fe(1)	C(6)	2.104(2)	C(11)	C(10)	1.384(3)
Fe(1)	C(5)	2.114(2)	C(4)	C(5)	1.416(4)
F(4)	C(19)	1.348(2)	C(4)	C(3)	1.421(3)
O(2)	C(2)	1.140(3)	C(7)	C(3)	1.405(3)
O(1)	C(1)	1.146(3)	C(7)	C(6)	1.417(4)
F(1)	C(15)	1.347(2)	C(5)	C(6)	1.409(4)

[1]-X,1-Y,-1-Z

Table 3.2 Bond Angles for 1__CpFe-TePh-DITFB.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(8)	Te(1)	Fe(1)	102.16(6)	C(13)	C(8)	C(9)	119.1(2)
C(1)	Fe(1)	C(2)	93.68(10)	C(13)	C(8)	Te(1)	121.64(16)
C(1)	Fe(1)	C(7)	118.98(10)	C(9)	C(8)	Te(1)	119.01(16)
C(2)	Fe(1)	C(7)	96.17(10)	F(4)	C(19)	C(15)[1]	118.80(19)
C(1)	Fe(1)	C(3)	91.73(10)	F(4)	C(19)	C(14)	119.70(19)
C(2)	Fe(1)	C(3)	128.66(10)	C(15)[1]	C(19)	C(14)	121.5(2)
C(7)	Fe(1)	C(3)	39.32(10)	C(19)	C(14)	C(15)	117.1(2)
C(1)	Fe(1)	C(4)	100.35(10)	C(19)	C(14)	I(1)	120.82(16)
C(2)	Fe(1)	C(4)	161.48(10)	C(15)	C(14)	I(1)	122.03(16)
C(7)	Fe(1)	C(4)	66.46(10)	C(8)	C(9)	C(10)	120.3(2)
C(3)	Fe(1)	C(4)	39.62(9)	C(11)	C(12)	C(13)	120.4(2)
C(1)	Fe(1)	C(6)	157.01(10)	C(12)	C(11)	C(10)	120.0(2)
C(2)	Fe(1)	C(6)	96.71(10)	C(5)	C(4)	C(3)	107.1(2)
C(7)	Fe(1)	C(6)	39.51(10)	C(5)	C(4)	Fe(1)	70.79(13)
C(3)	Fe(1)	C(6)	65.83(10)	C(3)	C(4)	Fe(1)	69.65(13)
C(4)	Fe(1)	C(6)	65.99(10)	F(1)	C(15)	C(19)[1]	118.84(19)
C(1)	Fe(1)	C(5)	137.09(11)	F(1)	C(15)	C(14)	119.74(19)
C(2)	Fe(1)	C(5)	129.11(11)	C(19)[1]	C(15)	C(14)	121.4(2)
C(7)	Fe(1)	C(5)	66.00(10)	C(3)	C(7)	C(6)	107.7(2)
C(3)	Fe(1)	C(5)	65.77(10)	C(3)	C(7)	Fe(1)	70.38(13)
C(4)	Fe(1)	C(5)	39.24(10)	C(6)	C(7)	Fe(1)	70.88(14)
C(6)	Fe(1)	C(5)	39.03(11)	C(11)	C(10)	C(9)	119.9(2)
C(1)	Fe(1)	Te(1)	91.27(7)	C(6)	C(5)	C(4)	108.4(2)
C(2)	Fe(1)	Te(1)	89.08(7)	C(6)	C(5)	Fe(1)	70.13(13)
C(7)	Fe(1)	Te(1)	148.73(7)	C(4)	C(5)	Fe(1)	69.98(13)
C(3)	Fe(1)	Te(1)	141.81(7)	C(5)	C(6)	C(7)	108.1(2)
C(4)	Fe(1)	Te(1)	102.54(7)	C(5)	C(6)	Fe(1)	70.84(14)
C(6)	Fe(1)	Te(1)	109.30(8)	C(7)	C(6)	Fe(1)	69.61(13)
C(5)	Fe(1)	Te(1)	86.83(7)	C(7)	C(3)	C(4)	108.7(2)
O(1)	C(1)	Fe(1)	176.0(2)	C(7)	C(3)	Fe(1)	70.30(13)
O(2)	C(2)	Fe(1)	178.2(2)	C(4)	C(3)	Fe(1)	70.73(13)
C(12)	C(13)	C(8)	120.3(2)				

[1]-X,1-Y,-1-Z

Complex 2 [CpFe(CO)(μ-SPh)]$_2$----*p*-DITFB

Table 4.1 Crystal data and structure refinement for 2__DITFB_CpFeSPh.

Identification code	2__DITFB_CpFeSPh
Empirical formula	$C_{15}H_{10}F_2FeIOS$
Formula weight	459.04
Temperature/K	150
Crystal system	triclinic
Space group	P-1
a/Å	10.6870(6)
b/Å	11.1135(7)
c/Å	14.7255(9)
α/°	83.6840(10)
β/°	77.2140(10)
γ/°	63.1560(10)
Volume/Å^3	1521.68(16)
Z	4
ρ_{calc}g/cm^3	2.004
μ/mm^{-1}	3.172
F(000)	884.0
Crystal size/mm^3	0.5 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.48 to 58
Index ranges	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -19 ≤ l ≤ 20
Reflections collected	17001
Independent reflections	8058 [R_{int} = 0.0366, R_{sigma} = 0.0601]
Data/restraints/parameters	8058/0/379
Goodness-of-fit on F^2	0.996
Final R indexes [I>=2σ (I)]	R_1 = 0.0370, wR_2 = 0.0651
Final R indexes [all data]	R_1 = 0.0619, wR_2 = 0.0731
Largest diff. peak/hole / e Å^{-3}	0.87/-1.18

Table 4.2 Bond Lengths for 2__DITFB_CpFeSPh.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Fe(1)	S(1)	2.2865(10)	C(9)	C(10)	1.403(6)
Fe(1)	S(2)	2.2619(10)	C(10)	C(11)	1.426(6)
Fe(1)	C(1)	1.753(4)	C(11)	C(12)	1.382(7)
Fe(1)	C(3)	2.102(4)	C(12A)	C(13)	1.388(6)
Fe(1)	C(4)	2.100(4)	C(12A)	C(15A)	1.391(5)
Fe(1)	C(5)	2.098(4)	C(13)	C(14)	1.368(7)
Fe(1)	C(6)	2.105(3)	C(14)	C(15)	1.380(7)
Fe(1)	C(7)	2.090(4)	C(15)	C(16)	1.379(6)
Fe(2)	S(1)	2.2823(10)	C(15A)	C(16)	1.387(5)
Fe(2)	S(2)	2.2584(10)	C(17)	C(18)	1.395(5)
Fe(2)	C(2)	1.756(4)	C(17)	C(22)	1.384(5)

Fe(2)	C(8)	2.100(4)	C(18)	C(19)	1.378(5)
Fe(2)	C(9)	2.099(4)	C(19)	C(20)	1.376(5)
Fe(2)	C(10)	2.093(4)	C(20)	C(21)	1.375(6)
Fe(2)	C(11)	2.088(4)	C(21)	C(22)	1.390(5)
Fe(2)	C(12)	2.093(4)	I(1)	C(1F)	2.105(3)
S(1)	C(15A)	1.791(4)	F(1)	C(6F)	1.351(4)
S(2)	C(17)	1.789(3)	F(2)	C(2F)	1.349(4)
O(1)	C(1)	1.150(4)	C(1F)	C(2F)	1.378(5)
O(2)	C(2)	1.152(4)	C(1F)	C(6F)	1.369(5)
C(3)	C(4)	1.399(5)	C(2F)	C(6F)[1]	1.381(5)
C(3)	C(7)	1.429(5)	I(2)	C(4F)	2.073(4)
C(4)	C(5)	1.419(5)	F(5)	C(9F)	1.340(4)
C(5)	C(6)	1.413(5)	F(6)	C(5F)	1.343(4)
C(6)	C(7)	1.403(5)	C(4F)	C(5F)	1.377(5)
C(8)	C(9)	1.408(6)	C(4F)	C(9F)	1.376(5)
C(8)	C(12)	1.396(6)	C(5F)	C(9F)[2]	1.383(5)

[1]2-X,2-Y,1-Z; [2]2-X,1-Y,1-Z

Table 4.3 Bond Angles for 2__DITFB_CpFeSPh.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S(2)	Fe(1)	S(1)	79.94(3)	C(4)	C(3)	Fe(1)	70.4(2)
C(1)	Fe(1)	S(1)	91.98(11)	C(4)	C(3)	C(7)	107.8(3)
C(1)	Fe(1)	S(2)	95.25(11)	C(7)	C(3)	Fe(1)	69.6(2)
C(1)	Fe(1)	C(3)	94.91(15)	C(3)	C(4)	Fe(1)	70.7(2)
C(1)	Fe(1)	C(4)	126.04(16)	C(3)	C(4)	C(5)	108.5(3)
C(1)	Fe(1)	C(5)	160.48(15)	C(5)	C(4)	Fe(1)	70.2(2)
C(1)	Fe(1)	C(6)	130.65(15)	C(4)	C(5)	Fe(1)	70.3(2)
C(1)	Fe(1)	C(7)	96.92(15)	C(6)	C(5)	Fe(1)	70.6(2)
C(3)	Fe(1)	S(1)	155.82(11)	C(6)	C(5)	C(4)	107.4(3)
C(3)	Fe(1)	S(2)	122.30(11)	C(5)	C(6)	Fe(1)	70.1(2)
C(3)	Fe(1)	C(6)	65.82(14)	C(7)	C(6)	Fe(1)	69.9(2)
C(4)	Fe(1)	S(1)	141.93(11)	C(7)	C(6)	C(5)	108.6(3)
C(4)	Fe(1)	S(2)	93.14(11)	C(3)	C(7)	Fe(1)	70.5(2)
C(4)	Fe(1)	C(3)	38.90(14)	C(6)	C(7)	Fe(1)	71.0(2)
C(4)	Fe(1)	C(6)	65.77(14)	C(6)	C(7)	C(3)	107.7(3)
C(5)	Fe(1)	S(1)	104.06(11)	C(9)	C(8)	Fe(2)	70.4(2)
C(5)	Fe(1)	S(2)	98.41(10)	C(12)	C(8)	Fe(2)	70.3(2)
C(5)	Fe(1)	C(3)	65.97(15)	C(12)	C(8)	C(9)	107.6(4)
C(5)	Fe(1)	C(4)	39.51(14)	C(8)	C(9)	Fe(2)	70.5(2)
C(5)	Fe(1)	C(6)	39.29(14)	C(10)	C(9)	Fe(2)	70.2(2)
C(6)	Fe(1)	S(1)	92.28(11)	C(10)	C(9)	C(8)	108.4(4)
C(6)	Fe(1)	S(2)	133.85(11)	C(9)	C(10)	Fe(2)	70.7(2)
C(7)	Fe(1)	S(1)	116.29(11)	C(9)	C(10)	C(11)	106.9(4)
C(7)	Fe(1)	S(2)	159.23(11)	C(11)	C(10)	Fe(2)	69.9(2)
C(7)	Fe(1)	C(3)	39.84(14)	C(10)	C(11)	Fe(2)	70.2(2)
C(7)	Fe(1)	C(4)	66.10(15)	C(12)	C(11)	Fe(2)	70.9(2)

C(7)	Fe(1)	C(5)	66.15(14)	C(12)	C(11)	C(10)	108.1(4)
C(7)	Fe(1)	C(6)	39.06(14)	C(8)	C(12)	Fe(2)	70.8(2)
S(2)	Fe(2)	S(1)	80.10(3)	C(11)	C(12)	Fe(2)	70.5(3)
C(2)	Fe(2)	S(1)	96.43(11)	C(11)	C(12)	C(8)	109.0(4)
C(2)	Fe(2)	S(2)	92.24(11)	C(13)	C(12A)	C(15A)	120.3(4)
C(2)	Fe(2)	C(8)	160.35(16)	C(14)	C(13)	C(12A)	120.7(5)
C(2)	Fe(2)	C(9)	131.94(16)	C(13)	C(14)	C(15)	119.1(4)
C(2)	Fe(2)	C(10)	97.82(16)	C(16)	C(15)	C(14)	121.0(5)
C(2)	Fe(2)	C(11)	95.15(17)	C(12A)	C(15A)	S(1)	121.8(3)
C(2)	Fe(2)	C(12)	125.69(18)	C(16)	C(15A)	S(1)	119.6(3)
C(8)	Fe(2)	S(1)	100.84(12)	C(16)	C(15A)	C(12A)	118.6(4)
C(8)	Fe(2)	S(2)	99.86(11)	C(15)	C(16)	C(15A)	120.2(4)
C(9)	Fe(2)	S(1)	90.94(11)	C(18)	C(17)	S(2)	120.6(3)
C(9)	Fe(2)	S(2)	135.76(12)	C(22)	C(17)	S(2)	120.0(3)
C(9)	Fe(2)	C(8)	39.19(15)	C(22)	C(17)	C(18)	119.2(3)
C(10)	Fe(2)	S(1)	117.29(14)	C(19)	C(18)	C(17)	120.0(4)
C(10)	Fe(2)	S(2)	158.50(14)	C(20)	C(19)	C(18)	120.6(4)
C(10)	Fe(2)	C(8)	65.90(16)	C(21)	C(20)	C(19)	119.8(4)
C(10)	Fe(2)	C(9)	39.12(15)	C(20)	C(21)	C(22)	120.3(4)
C(10)	Fe(2)	C(12)	65.78(18)	C(17)	C(22)	C(21)	120.0(4)
C(11)	Fe(2)	S(1)	155.89(13)	C(2F)	C(1F)	I(1)	120.6(2)
C(11)	Fe(2)	S(2)	120.50(15)	C(6F)	C(1F)	I(1)	121.7(3)
C(11)	Fe(2)	C(8)	65.37(17)	C(6F)	C(1F)	C(2F)	117.6(3)
C(11)	Fe(2)	C(9)	65.73(16)	F(2)	C(2F)	C(1F)	120.7(3)
C(11)	Fe(2)	C(10)	39.87(18)	F(2)	C(2F)	C(6F)[1]	118.4(3)
C(11)	Fe(2)	C(12)	38.60(18)	C(1F)	C(2F)	C(6F)[1]	120.9(3)
C(12)	Fe(2)	S(1)	137.67(15)	F(1)	C(6F)	C(1F)	119.6(3)
C(12)	Fe(2)	S(2)	92.94(13)	F(1)	C(6F)	C(2F)[1]	118.9(3)
C(12)	Fe(2)	C(8)	38.89(17)	C(1F)	C(6F)	C(2F)[1]	121.5(3)
C(12)	Fe(2)	C(9)	65.33(16)	C(5F)	C(4F)	I(2)	121.3(3)
Fe(2)	S(1)	Fe(1)	97.54(4)	C(9F)	C(4F)	I(2)	121.4(3)
C(15A)	S(1)	Fe(1)	109.25(12)	C(9F)	C(4F)	C(5F)	117.3(3)
C(15A)	S(1)	Fe(2)	112.70(13)	F(6)	C(5F)	C(4F)	119.8(4)
Fe(2)	S(2)	Fe(1)	98.95(4)	F(6)	C(5F)	C(9F)[2]	118.7(4)
C(17)	S(2)	Fe(1)	112.71(12)	C(4F)	C(5F)	C(9F)[2]	121.5(3)
C(17)	S(2)	Fe(2)	112.38(12)	F(5)	C(9F)	C(4F)	120.8(4)
O(1)	C(1)	Fe(1)	178.3(3)	F(5)	C(9F)	C(5F)[2]	118.0(4)
O(2)	C(2)	Fe(2)	177.7(3)	C(4F)	C(9F)	C(5F)[2]	121.2(4)

[1]2-X,2-Y,1-Z; [2]2-X,1-Y,1-Z

Complex 3 $CpFe(CO)_2Cl$----*p*-DITFB

Table 5.1 Crystal data and structure refinement for 3__DITFB_CpFeCl.

Identification code	3__DITFB_CpFeCl
Empirical formula	$C_{13}H_5ClF_4FeI_2O_2$
Formula weight	614.27
Temperature/K	423(2)
Crystal system	Orthorhombic
Space group	Pbca
a/Å	19.16(3)
b/Å	7.157(11)
c/Å	24.99(4)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	3426(9)
Z	8
$\rho_{calc}g/cm^3$	2.382
μ/mm^{-1}	4.682
F(000)	2272.0
Crystal size/mm^3	0.600 × 0.200 × 0.200
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.26 to 57.986
Index ranges	$-26 \le h \le 25$, $-9 \le k \le 9$, $-33 \le l \le 34$
Reflections collected	25857
Independent reflections	4542 [R_{int} = 0.0488, R_{sigma} = 0.0340]
Data/restraints/parameters	4542/0/208
Goodness-of-fit on F^2	1.009
Final R indexes [I>=2σ (I)]	R_1 = 0.0290, wR_2 = 0.0561
Final R indexes [all data]	R_1 = 0.0491, wR_2 = 0.0631
Largest diff. peak/hole / e $Å^{-3}$	0.74/-0.52

Table 5.2 Bond Lengths for 3__DITFB_CpFeCl.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I(1)	C(8)	2.103(4)	C(8)	C(9)	1.383(5)
I(2)	C(11)	2.104(4)	C(8)	C(13)	1.397(5)
Fe(1)	C(1)	1.801(4)	O(1)	C(1)	1.144(4)
Fe(1)	C(2)	1.814(4)	C(2)	O(2)	1.137(5)
Fe(1)	C(4)	2.102(5)	C(13)	C(12)	1.382(5)
Fe(1)	C(5)	2.102(5)	C(11)	C(10)	1.389(5)
Fe(1)	C(6)	2.119(4)	C(11)	C(12)	1.396(5)
Fe(1)	C(3)	2.124(5)	C(10)	C(9)	1.390(5)
Fe(1)	C(7)	2.130(5)	C(6)	C(7)	1.410(6)
Fe(1)	Cl(1)	2.318(3)	C(6)	C(5)	1.425(6)

F(4)	C(13)	1.363(4)	C(7)	C(3)	1.411(6)
F(2)	C(10)	1.357(4)	C(3)	C(4)	1.431(6)
F(3)	C(12)	1.355(4)	C(4)	C(5)	1.408(6)
F(1)	C(9)	1.357(4)			

Table 5.3 Bond Angles for 3__DITFB_CpFeCl.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(1)	Fe(1)	C(2)	95.5(2)	O(1)	C(1)	Fe(1)	177.7(4)
C(1)	Fe(1)	C(4)	120.26(18)	F(4)	C(13)	C(12)	117.8(3)
C(2)	Fe(1)	C(4)	92.3(2)	F(4)	C(13)	C(8)	120.0(3)
C(1)	Fe(1)	C(5)	90.81(19)	C(12)	C(13)	C(8)	122.2(3)
C(2)	Fe(1)	C(5)	122.82(18)	C(10)	C(11)	C(12)	116.6(3)
C(4)	Fe(1)	C(5)	39.14(17)	C(10)	C(11)	I(2)	120.7(3)
C(1)	Fe(1)	C(6)	97.36(19)	C(12)	C(11)	I(2)	122.7(3)
C(2)	Fe(1)	C(6)	157.99(18)	F(2)	C(10)	C(11)	120.2(3)
C(4)	Fe(1)	C(6)	65.77(19)	F(2)	C(10)	C(9)	118.0(3)
C(5)	Fe(1)	C(6)	39.47(17)	C(11)	C(10)	C(9)	121.8(3)
C(1)	Fe(1)	C(3)	156.76(17)	F(3)	C(12)	C(13)	118.6(3)
C(2)	Fe(1)	C(3)	96.7(2)	F(3)	C(12)	C(11)	120.1(3)
C(4)	Fe(1)	C(3)	39.58(17)	C(13)	C(12)	C(11)	121.3(3)
C(5)	Fe(1)	C(3)	65.97(19)	C(7)	C(6)	C(5)	107.7(4)
C(6)	Fe(1)	C(3)	65.52(19)	C(7)	C(6)	Fe(1)	71.1(2)
C(1)	Fe(1)	C(7)	133.03(18)	C(5)	C(6)	Fe(1)	69.6(2)
C(2)	Fe(1)	C(7)	131.42(18)	C(6)	C(7)	C(3)	108.9(4)
C(4)	Fe(1)	C(7)	65.44(19)	C(6)	C(7)	Fe(1)	70.2(2)
C(5)	Fe(1)	C(7)	65.48(19)	C(3)	C(7)	Fe(1)	70.4(2)
C(6)	Fe(1)	C(7)	38.76(16)	C(7)	C(3)	C(4)	107.2(4)
C(3)	Fe(1)	C(7)	38.75(16)	C(7)	C(3)	Fe(1)	70.9(2)
C(1)	Fe(1)	Cl(1)	90.28(15)	C(4)	C(3)	Fe(1)	69.4(2)
C(2)	Fe(1)	Cl(1)	90.41(16)	F(1)	C(9)	C(8)	120.3(3)
C(4)	Fe(1)	Cl(1)	148.87(13)	F(1)	C(9)	C(10)	117.9(3)
C(5)	Fe(1)	Cl(1)	146.46(13)	C(8)	C(9)	C(10)	121.8(3)
C(6)	Fe(1)	Cl(1)	107.25(15)	C(5)	C(4)	C(3)	108.3(4)
C(3)	Fe(1)	Cl(1)	109.31(16)	C(5)	C(4)	Fe(1)	70.4(2)
C(7)	Fe(1)	Cl(1)	89.93(17)	C(3)	C(4)	Fe(1)	71.0(2)
C(9)	C(8)	C(13)	116.3(3)	C(4)	C(5)	C(6)	108.0(4)
C(9)	C(8)	I(1)	121.4(3)	C(4)	C(5)	Fe(1)	70.4(2)
C(13)	C(8)	I(1)	122.2(3)	C(6)	C(5)	Fe(1)	70.9(2)
O(2)	C(2)	Fe(1)	179.0(4)				

Complex 4 $CpFe(CO)_2Br$----*p*-DITFB

Table 6.1 Crystal data and structure refinement for 4__DITFB_CpFeBr.

Identification code	4__DITFB_CpFeBr
Empirical formula	$C_{13}H_5BrF_4FeI_2O_2$
Formula weight	658.73
Temperature/K	423(2)
Crystal system	Orthorhombic
Space group	Pbca
a/Å	19.1299(9)
b/Å	7.1259(3)
c/Å	25.1867(12)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	3433.4(3)
Z	8
$\rho_{calc}g/cm^3$	2.549
μ/mm^{-1}	6.844
F(000)	2416.0
Crystal size/mm^3	0.800 × 0.500 × 0.200
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.348 to 57.994
Index ranges	$-25 \leq h \leq 26$, $-9 \leq k \leq 9$, $-34 \leq l \leq 34$
Reflections collected	33312
Independent reflections	4547 [R_{int} = 0.0358, R_{sigma} = 0.0216]
Data/restraints/parameters	4547/0/208
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0227, wR_2 = 0.0468
Final R indexes [all data]	R_1 = 0.0316, wR_2 = 0.0499
Largest diff. peak/hole / e $Å^{-3}$	0.85/-0.87

Table 6.2 Bond Lengths for 4__DITFB_CpFeBr.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I(1)	C(8)	2.089(2)	Fe(1)	C(2)	1.787(3)
I(2)	C(11)	2.092(2)	Fe(1)	C(3)	2.072(3)
F(1)	C(9)	1.344(3)	Fe(1)	C(4)	2.073(3)
F(2)	C(10)	1.344(3)	Fe(1)	C(5)	2.088(3)
F(3)	C(12)	1.346(3)	Fe(1)	C(7)	2.095(3)
F(4)	C(13)	1.347(3)	Fe(1)	C(6)	2.107(3)
C(8)	C(9)	1.374(4)	O(1)	C(1)	1.141(4)
C(8)	C(13)	1.385(4)	O(2)	C(2)	1.136(4)
C(9)	C(10)	1.383(4)	C(3)	C(4)	1.403(4)
C(10)	C(11)	1.379(4)	C(3)	C(7)	1.419(5)
C(11)	C(12)	1.386(4)	C(4)	C(5)	1.410(5)

C(12)	C(13)	1.379(4)	C(5)	C(6)	1.405(5)
Br(1)	Fe(1)	2.4196(5)	C(6)	C(7)	1.398(5)
Fe(1)	C(1)	1.783(3)			

Table 6.3 Bond Angles for 4__DITFB_CpFeBr.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(9)	C(8)	C(13)	117.0(2)	C(5)	Fe(1)	C(7)	66.15(13)
C(9)	C(8)	I(1)	120.30(19)	C(1)	Fe(1)	C(6)	130.26(14)
C(13)	C(8)	I(1)	122.7(2)	C(2)	Fe(1)	C(6)	133.54(13)
F(1)	C(9)	C(8)	120.4(2)	C(3)	Fe(1)	C(6)	65.83(15)
F(1)	C(9)	C(10)	118.0(2)	C(4)	Fe(1)	C(6)	65.65(14)
C(8)	C(9)	C(10)	121.6(2)	C(5)	Fe(1)	C(6)	39.13(13)
F(2)	C(10)	C(11)	120.4(2)	C(7)	Fe(1)	C(6)	38.85(13)
F(2)	C(10)	C(9)	118.0(2)	C(1)	Fe(1)	Br(1)	90.18(10)
C(11)	C(10)	C(9)	121.5(2)	C(2)	Fe(1)	Br(1)	89.76(10)
C(10)	C(11)	C(12)	116.9(2)	C(3)	Fe(1)	Br(1)	149.63(10)
C(10)	C(11)	I(2)	121.23(19)	C(4)	Fe(1)	Br(1)	145.83(10)
C(12)	C(11)	I(2)	121.87(19)	C(5)	Fe(1)	Br(1)	106.53(10)
F(3)	C(12)	C(13)	118.3(2)	C(7)	Fe(1)	Br(1)	109.84(10)
F(3)	C(12)	C(11)	120.3(2)	C(6)	Fe(1)	Br(1)	89.95(10)
C(13)	C(12)	C(11)	121.4(2)	O(1)	C(1)	Fe(1)	178.6(3)
F(4)	C(13)	C(12)	118.1(2)	O(2)	C(2)	Fe(1)	177.6(3)
F(4)	C(13)	C(8)	120.4(2)	C(4)	C(3)	C(7)	107.7(3)
C(12)	C(13)	C(8)	121.5(2)	C(4)	C(3)	Fe(1)	70.23(18)
C(1)	Fe(1)	C(2)	96.20(14)	C(7)	C(3)	Fe(1)	70.97(19)
C(1)	Fe(1)	C(3)	92.12(14)	C(3)	C(4)	C(5)	108.5(3)
C(2)	Fe(1)	C(3)	120.03(14)	C(3)	C(4)	Fe(1)	70.21(18)
C(1)	Fe(1)	C(4)	123.70(14)	C(5)	C(4)	Fe(1)	70.77(18)
C(2)	Fe(1)	C(4)	90.70(14)	C(6)	C(5)	C(4)	107.2(3)
C(3)	Fe(1)	C(4)	39.57(13)	C(6)	C(5)	Fe(1)	71.16(18)
C(1)	Fe(1)	C(5)	158.46(14)	C(4)	C(5)	Fe(1)	69.61(18)
C(2)	Fe(1)	C(5)	97.34(13)	C(7)	C(6)	C(5)	109.1(3)
C(3)	Fe(1)	C(5)	66.57(13)	C(7)	C(6)	Fe(1)	70.14(19)
C(4)	Fe(1)	C(5)	39.62(14)	C(5)	C(6)	Fe(1)	69.71(18)
C(1)	Fe(1)	C(7)	95.75(14)	C(6)	C(7)	C(3)	107.5(3)
C(2)	Fe(1)	C(7)	156.95(14)	C(6)	C(7)	Fe(1)	71.00(19)
C(3)	Fe(1)	C(7)	39.81(14)	C(3)	C(7)	Fe(1)	69.22(18)
C(4)	Fe(1)	C(7)	66.29(13)				

Complex 5 $CpFe(CO)_2I$----*p*-DITFB

Table 7.1 Crystal data and structure refinement for 5.

Identification code	1
Empirical formula	$C_{10}H_5F_2FeI_2O_2$
Formula weight	504.79
Temperature/K	150.0
Crystal system	triclinic
Space group	P-1
a/Å	8.0151(4)
b/Å	8.2003(5)
c/Å	10.3911(6)
α/°	105.4770(10)
β/°	93.4690(10)
γ/°	95.4210(10)
Volume/$Å^3$	652.64(6)
Z	2
$\rho_{calc}g/cm^3$	2.569
μ/mm^{-1}	5.895
F(000)	462.0
Crystal size/mm^3	0.4 × 0.4 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.126 to 58
Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-14 \leq l \leq 14$
Reflections collected	6084
Independent reflections	3371 [R_{int} = 0.0258, R_{sigma} = 0.0365]
Data/restraints/parameters	3371/0/154
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0258, wR_2 = 0.0654
Final R indexes [all data]	R_1 = 0.0275, wR_2 = 0.0665
Largest diff. peak/hole / e $Å^{-3}$	0.69/-1.75

Table 7.2 Bond Lengths for 5.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I(2)	C(8)	2.090(3)	O(2)	C(2)	1.136(4)
I(1)	Fe(1)	2.6025(4)	C(10)	$C(9)^1$	1.375(4)
Fe(1)	C(1)	1.782(3)	C(10)	C(8)	1.375(4)
Fe(1)	C(2)	1.775(3)	C(10)	F(2)	1.347(3)
Fe(1)	C(6)	2.071(3)	C(9)	C(8)	1.395(3)
Fe(1)	C(5)	2.073(3)	C(6)	C(5)	1.401(5)
Fe(1)	C(4)	2.091(3)	C(6)	C(7)	1.421(5)
Fe(1)	C(3)	2.115(3)	C(5)	C(4)	1.422(5)
Fe(1)	C(7)	2.106(3)	C(4)	C(3)	1.418(5)
F(1)	C(9)	1.345(3)	C(3)	C(7)	1.397(5)
C(1)	O(1)	1.138(4)			

[1]2-X,1-Y,1-Z

Table 7.3 Bond Angles for 5.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(1)	Fe(1)	I(1)	92.30(10)	C(7)	Fe(1)	C(3)	38.65(14)
C(1)	Fe(1)	C(6)	93.70(14)	O(1)	C(1)	Fe(1)	177.2(3)
C(1)	Fe(1)	C(5)	127.59(15)	C(9)[1]	C(10)	C(8)	121.9(2)
C(1)	Fe(1)	C(4)	158.44(14)	F(2)	C(10)	C(9)[1]	118.2(2)
C(1)	Fe(1)	C(3)	125.29(15)	F(2)	C(10)	C(8)	119.9(2)
C(1)	Fe(1)	C(7)	93.05(14)	O(2)	C(2)	Fe(1)	177.6(3)
C(2)	Fe(1)	I(1)	90.21(9)	F(1)	C(9)	C(10)[1]	118.6(2)
C(2)	Fe(1)	C(1)	93.87(16)	F(1)	C(9)	C(8)	120.4(3)
C(2)	Fe(1)	C(6)	114.95(13)	C(10)[1]	C(9)	C(8)	120.9(2)
C(2)	Fe(1)	C(5)	90.13(14)	C(10)	C(8)	I(2)	122.05(19)
C(2)	Fe(1)	C(4)	102.58(16)	C(10)	C(8)	C(9)	117.1(3)
C(2)	Fe(1)	C(3)	140.80(16)	C(9)	C(8)	I(2)	120.8(2)
C(2)	Fe(1)	C(7)	154.23(13)	C(5)	C(6)	Fe(1)	70.32(17)
C(6)	Fe(1)	I(1)	153.61(9)	C(5)	C(6)	C(7)	107.9(3)
C(6)	Fe(1)	C(5)	39.51(15)	C(7)	C(6)	Fe(1)	71.42(17)
C(6)	Fe(1)	C(4)	66.83(14)	C(6)	C(5)	Fe(1)	70.18(18)
C(6)	Fe(1)	C(3)	65.85(12)	C(6)	C(5)	C(4)	108.6(3)
C(6)	Fe(1)	C(7)	39.76(13)	C(4)	C(5)	Fe(1)	70.72(17)
C(5)	Fe(1)	I(1)	139.98(11)	C(5)	C(4)	Fe(1)	69.35(18)
C(5)	Fe(1)	C(4)	39.93(15)	C(3)	C(4)	Fe(1)	71.22(18)
C(5)	Fe(1)	C(3)	65.88(13)	C(3)	C(4)	C(5)	106.7(3)
C(5)	Fe(1)	C(7)	66.18(13)	C(4)	C(3)	Fe(1)	69.39(18)
C(4)	Fe(1)	I(1)	101.38(10)	C(7)	C(3)	Fe(1)	70.30(17)
C(4)	Fe(1)	C(3)	39.39(15)	C(7)	C(3)	C(4)	109.0(3)
C(4)	Fe(1)	C(7)	66.19(14)	C(6)	C(7)	Fe(1)	68.82(16)
C(3)	Fe(1)	I(1)	89.86(9)	C(3)	C(7)	Fe(1)	71.06(18)
C(7)	Fe(1)	I(1)	114.27(9)	C(3)	C(7)	C(6)	107.8(3)

[1]2-X,1-Y,1-Z

Complex 6 $(Me_4C_4)Co(CO)_2I$----*p*-DITFB

Table 8.1 Crystal data and structure refinement for 6.

Identification code	6__DITFB_CbCoCO2I
Empirical formula	$C_{16}H_{12}CoF_4I_3O_2$
Formula weight	751.89
Temperature/K	100(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	14.137(5)
b/Å	10.691(3)
c/Å	13.803(4)
α/°	90
β/°	95.373(5)
γ/°	90
Volume/Å^3	2077.0(11)
Z	4
ρ_{calc}g/cm^3	2.405
μ/mm^{-1}	5.327
F(000)	1384.0
Crystal size/mm^3	0.500 × 0.200 × 0.050
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.894 to 57.994
Index ranges	$-19 \le h \le 19$, $0 \le k \le 14$, $0 \le l \le 18$
Reflections collected	5517
Independent reflections	5517 [R_{int} = ?, R_{sigma} = 0.0307]
Data/restraints/parameters	5517/0/240
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0383, wR_2 = 0.0953
Final R indexes [all data]	R_1 = 0.0430, wR_2 = 0.1021
Largest diff. peak/hole / e Å^{-3}	4.72/-1.75

Table 8.2 Bond Lengths for 6__DITFB_CbCoCO2I.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I(2)	C(11)	2.108(6)	Co(1)	C(4)	2.035(6)
I(3)	C(14)	2.093(7)	Co(1)	C(3)	2.037(7)
F(1)	C(12)	1.352(8)	Co(1)	C(5)	2.049(7)
F(2)	C(13)	1.335(8)	Co(1)	C(6)	2.067(7)
F(3)	C(15)	1.338(8)	O(1)	C(1)	1.117(10)
F(4)	C(16)	1.351(8)	O(2)	C(2)	1.112(10)
C(11)	C(12)	1.355(10)	C(3)	C(6)	1.446(10)
C(11)	C(16)	1.404(9)	C(3)	C(4)	1.465(9)
C(12)	C(13)	1.397(9)	C(3)	C(7)	1.517(10)
C(13)	C(14)	1.411(9)	C(4)	C(5)	1.456(10)
C(14)	C(15)	1.373(10)	C(4)	C(8)	1.517(10)
C(15)	C(16)	1.398(9)	C(5)	C(6)	1.453(10)

I(1)	Co(1)	2.6189(12)	C(5)	C(9)	1.481(10)
Co(1)	C(1)	1.826(8)	C(6)	C(10)	1.478(10)
Co(1)	C(2)	1.832(8)			

Table 8.3 Bond Angles for 6__DITFB_CbCoCO2I.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(12)	C(11)	C(16)	118.7(6)	C(1)	Co(1)	I(1)	94.8(3)
C(12)	C(11)	I(2)	123.0(5)	C(2)	Co(1)	I(1)	97.4(3)
C(16)	C(11)	I(2)	118.4(5)	C(4)	Co(1)	I(1)	97.1(2)
F(1)	C(12)	C(11)	120.4(6)	C(3)	Co(1)	I(1)	94.7(2)
F(1)	C(12)	C(13)	118.0(6)	C(5)	Co(1)	I(1)	138.5(2)
C(11)	C(12)	C(13)	121.5(6)	C(6)	Co(1)	I(1)	134.5(2)
F(2)	C(13)	C(12)	118.1(6)	O(1)	C(1)	Co(1)	178.6(8)
F(2)	C(13)	C(14)	121.7(6)	O(2)	C(2)	Co(1)	176.9(8)
C(12)	C(13)	C(14)	120.2(6)	C(6)	C(3)	C(4)	89.9(6)
C(15)	C(14)	C(13)	118.2(6)	C(6)	C(3)	C(7)	133.3(6)
C(15)	C(14)	I(3)	123.0(5)	C(4)	C(3)	C(7)	134.4(7)
C(13)	C(14)	I(3)	118.8(5)	C(6)	C(3)	Co(1)	70.5(4)
F(3)	C(15)	C(14)	120.0(6)	C(4)	C(3)	Co(1)	68.8(4)
F(3)	C(15)	C(16)	119.0(6)	C(7)	C(3)	Co(1)	131.1(5)
C(14)	C(15)	C(16)	121.0(6)	C(5)	C(4)	C(3)	89.6(6)
F(4)	C(16)	C(15)	117.7(6)	C(5)	C(4)	C(8)	133.5(7)
F(4)	C(16)	C(11)	121.9(6)	C(3)	C(4)	C(8)	135.0(6)
C(15)	C(16)	C(11)	120.4(6)	C(5)	C(4)	Co(1)	69.6(4)
C(1)	Co(1)	C(2)	98.0(3)	C(3)	C(4)	Co(1)	69.0(4)
C(1)	Co(1)	C(4)	151.4(3)	C(8)	C(4)	Co(1)	130.2(5)
C(2)	Co(1)	C(4)	106.1(3)	C(6)	C(5)	C(4)	90.0(6)
C(1)	Co(1)	C(3)	111.0(3)	C(6)	C(5)	C(9)	133.7(7)
C(2)	Co(1)	C(3)	147.4(3)	C(4)	C(5)	C(9)	134.1(7)
C(4)	Co(1)	C(3)	42.2(3)	C(6)	C(5)	Co(1)	70.0(4)
C(1)	Co(1)	C(5)	124.1(3)	C(4)	C(5)	Co(1)	68.6(4)
C(2)	Co(1)	C(5)	91.3(3)	C(9)	C(5)	Co(1)	131.2(5)
C(4)	Co(1)	C(5)	41.8(3)	C(3)	C(6)	C(5)	90.5(6)
C(3)	Co(1)	C(5)	60.5(3)	C(3)	C(6)	C(10)	134.7(7)
C(1)	Co(1)	C(6)	93.3(3)	C(5)	C(6)	C(10)	133.8(7)
C(2)	Co(1)	C(6)	125.5(3)	C(3)	C(6)	Co(1)	68.3(4)
C(4)	Co(1)	C(6)	60.2(3)	C(5)	C(6)	Co(1)	68.7(4)
C(3)	Co(1)	C(6)	41.2(3)	C(10)	C(6)	Co(1)	129.2(5)
C(5)	Co(1)	C(6)	41.3(3)				

Complex 7 $(Me_4C_4)Co(CO)_2I$

Table 9.1 Crystal data and structure refinement for 7

Identification code	7__CbCOCO2I
Empirical formula	$C_{10}H_{12}CoIO_2$
Formula weight	350.03
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.066(4)
b/Å	13.931(4)
c/Å	14.062(4)
α/°	90
β/°	117.280(5)
γ/°	90
Volume/Å^3	2449.1(13)
Z	8
ρ_{calc}g/cm^3	1.899
μ/mm^{-1}	3.896
F(000)	1344.0
Crystal size/mm^3	0.400 × 0.200 × 0.100
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.258 to 52.962
Index ranges	$-17 \le h \le 15$, $0 \le k \le 17$, $0 \le l \le 17$
Reflections collected	5093
Independent reflections	5093 [R_{int} = ?, R_{sigma} = 0.0729]
Data/restraints/parameters	5093/0/262
Goodness-of-fit on F^2	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0489, wR_2 = 0.0901
Final R indexes [all data]	R_1 = 0.0796, wR_2 = 0.1028
Largest diff. peak/hole / e Å^{-3}	1.13/-1.34

Table 9.2 Bond Lengths for 7__CbCOCO2I.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I(1)	Co(1)	2.6062(12)	C(4)	C(8)	1.482(10)
I(2)	Co(2)	2.5979(13)	O(2)	C(2)	1.157(10)
Co(2)	C(15)	1.992(7)	C(5)	C(6)	1.442(10)
Co(2)	C(2AA)	2.046(8)	C(5)	C(9)	1.496(11)
Co(2)	C(13)	2.099(8)	O(4)	C(12)	1.143(10)
Co(2)	C(11)	1.780(8)	C(15)	C(2AA)	1.437(11)
Co(2)	C(14)	2.019(9)	C(15)	C(13)	2.039(11)
Co(2)	C(12)	1.775(9)	C(15)	C(14)	1.467(11)
Co(1)	C(4)	2.026(7)	C(15)	C(18)	1.476(10)
Co(1)	C(5)	2.033(8)	C(2AA)	C(13)	1.436(11)
Co(1)	C(3)	2.040(8)	C(2AA)	C(14)	2.031(11)
Co(1)	C(6)	2.051(7)	C(2AA)	C(19)	1.489(11)
Co(1)	C(1)	1.786(9)	C(3)	C(6)	1.434(11)
Co(1)	C(2)	1.781(9)	C(3)	C(7)	1.487(11)

O(1)	C(1)	1.162(10)	C(6)	C(10)	1.481(11)
O(3)	C(11)	1.146(9)	C(13)	C(14)	1.417(12)
C(4)	C(5)	1.445(10)	C(13)	C(16)	1.484(11)
C(4)	C(3)	1.465(10)	C(14)	C(17)	1.486(11)

Table 9.3 Bond Angles for 7__CbCOCO2I.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(15)	Co(2)	I(2)	148.4(2)	C(2AA)	C(15)	Co(2)	71.2(4)
C(15)	Co(2)	C(2AA)	41.7(3)	C(2AA)	C(15)	C(13)	44.8(4)
C(15)	Co(2)	C(13)	59.7(3)	C(2AA)	C(15)	C(14)	88.8(6)
C(15)	Co(2)	C(14)	42.9(3)	C(2AA)	C(15)	C(18)	133.2(7)
C(2AA)	Co(2)	I(2)	124.1(2)	C(14)	C(15)	Co(2)	69.6(4)
C(2AA)	Co(2)	C(13)	40.5(3)	C(14)	C(15)	C(13)	44.0(4)
C(13)	Co(2)	I(2)	92.0(2)	C(14)	C(15)	C(18)	136.5(8)
C(11)	Co(2)	I(2)	94.7(3)	C(18)	C(15)	Co(2)	127.4(5)
C(11)	Co(2)	C(15)	111.9(3)	C(18)	C(15)	C(13)	169.8(6)
C(11)	Co(2)	C(2AA)	92.5(3)	C(15)	C(2AA)	Co(2)	67.2(4)
C(11)	Co(2)	C(13)	122.4(4)	C(15)	C(2AA)	C(14)	46.2(4)
C(11)	Co(2)	C(14)	151.5(3)	C(15)	C(2AA)	C(19)	133.4(7)
C(14)	Co(2)	I(2)	106.6(2)	C(13)	C(2AA)	Co(2)	71.7(4)
C(14)	Co(2)	C(2AA)	59.9(3)	C(13)	C(2AA)	C(15)	90.4(6)
C(14)	Co(2)	C(13)	40.2(3)	C(13)	C(2AA)	C(14)	44.2(5)
C(12)	Co(2)	I(2)	94.5(3)	C(13)	C(2AA)	C(19)	134.4(8)
C(12)	Co(2)	C(15)	96.2(4)	C(14)	C(2AA)	Co(2)	59.4(3)
C(12)	Co(2)	C(2AA)	137.5(4)	C(19)	C(2AA)	Co(2)	129.8(6)
C(12)	Co(2)	C(13)	134.1(4)	C(19)	C(2AA)	C(14)	170.8(7)
C(12)	Co(2)	C(11)	102.3(4)	C(4)	C(3)	Co(1)	68.4(4)
C(12)	Co(2)	C(14)	94.9(4)	C(4)	C(3)	C(7)	135.7(8)
C(4)	Co(1)	I(1)	98.9(2)	C(6)	C(3)	Co(1)	69.9(4)
C(4)	Co(1)	C(5)	41.7(3)	C(6)	C(3)	C(4)	89.6(7)
C(4)	Co(1)	C(3)	42.2(3)	C(6)	C(3)	C(7)	132.7(7)
C(4)	Co(1)	C(6)	60.2(3)	C(7)	C(3)	Co(1)	130.9(6)
C(5)	Co(1)	I(1)	140.5(2)	C(5)	C(6)	Co(1)	68.7(4)
C(5)	Co(1)	C(3)	60.4(3)	C(5)	C(6)	C(10)	134.0(8)
C(5)	Co(1)	C(6)	41.4(3)	C(3)	C(6)	Co(1)	69.1(4)
C(3)	Co(1)	I(1)	94.3(2)	C(3)	C(6)	C(5)	90.8(6)
C(3)	Co(1)	C(6)	41.0(3)	C(3)	C(6)	C(10)	134.0(8)
C(6)	Co(1)	I(1)	133.2(2)	C(10)	C(6)	Co(1)	129.2(6)
C(1)	Co(1)	I(1)	95.5(3)	C(15)	C(13)	Co(2)	57.5(3)
C(1)	Co(1)	C(4)	149.9(3)	C(2AA)	C(13)	Co(2)	67.7(4)
C(1)	Co(1)	C(5)	120.7(3)	C(2AA)	C(13)	C(15)	44.8(5)
C(1)	Co(1)	C(3)	110.6(3)	C(2AA)	C(13)	C(16)	134.6(9)
C(1)	Co(1)	C(6)	90.8(3)	C(14)	C(13)	Co(2)	66.9(5)
C(2)	Co(1)	I(1)	94.3(3)	C(14)	C(13)	C(15)	46.0(4)
C(2)	Co(1)	C(4)	103.7(4)	C(14)	C(13)	C(2AA)	90.8(6)
C(2)	Co(1)	C(5)	93.3(4)	C(14)	C(13)	C(16)	134.0(9)
C(2)	Co(1)	C(3)	145.8(4)	C(16)	C(13)	Co(2)	129.5(6)

C(2)	Co(1)	C(6)	129.8(4)	C(16)	C(13)	C(15)	173.0(6)
C(2)	Co(1)	C(1)	101.4(4)	O(1)	C(1)	Co(1)	178.1(8)
C(5)	C(4)	Co(1)	69.4(4)	O(3)	C(11)	Co(2)	179.1(8)
C(5)	C(4)	C(3)	89.5(6)	Co(2)	C(14)	C(2AA)	60.7(3)
C(5)	C(4)	C(8)	133.0(7)	C(15)	C(14)	Co(2)	67.5(4)
C(3)	C(4)	Co(1)	69.4(5)	C(15)	C(14)	C(2AA)	45.0(4)
C(3)	C(4)	C(8)	135.9(8)	C(15)	C(14)	C(17)	132.6(8)
C(8)	C(4)	Co(1)	129.3(5)	C(13)	C(14)	Co(2)	72.9(5)
C(4)	C(5)	Co(1)	68.9(4)	C(13)	C(14)	C(15)	90.0(6)
C(4)	C(5)	C(9)	133.4(7)	C(13)	C(14)	C(2AA)	45.0(5)
C(6)	C(5)	Co(1)	70.0(5)	C(13)	C(14)	C(17)	135.7(8)
C(6)	C(5)	C(4)	90.1(7)	C(17)	C(14)	Co(2)	128.3(7)
C(6)	C(5)	C(9)	134.9(7)	C(17)	C(14)	C(2AA)	170.8(8)
C(9)	C(5)	Co(1)	129.6(6)	O(2)	C(2)	Co(1)	179.7(10)
Co(2)	C(15)	C(13)	62.8(3)	O(4)	C(12)	Co(2)	179.2(9)