Supplementary Material (ESI) for Chemical Communications

Novel catalysts for dechlorination of polychlorinated biphenyls (PCBs) and other chlorinated aromatics

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ELECTRONIC SUPPLEMENTARY DATA

Table 1: Crystal data and refinement details for $2[BF_4]_2$

Crystal identification	ARC1514
Chemical formula	$C_{32}H_{38}B_2F_8Fe_2$
Formula weight	707.95
Temperature (K)	150
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P\,2_1/n$
a (Å)	9.5417(3)
b (Å)	26.6042(10)
c (Å)	12.3888(4)
α (°)	90
β (°)	107.7721(7)
γ (°)	90
Cell volume (Å^3)	2994.81(18)
Z	4
Calculated density (Mg/m^3)	1.570
Absorption coefficient (mm^{-1})	1.041
F_{000}	1456
Crystal size (mm)	0.06 x 0.08 x 0.26
Description of crystal	Orange prism
Absorption correction	Semi-empirical from equivalent reflections
Transmission coefficients (min,max)	0.76, 0.94
θ range for data collection (°)	$5.0 \leq \theta \leq 27.5$
Index ranges	$-12 \leq h \leq 11$, $0 \leq k \leq 34$, $0 \leq l \leq 15$
Reflections measured	23181
Unique reflections	6378
R_{int}	0.063
Observed reflections ($I > 3\sigma(I)$)	3965
Refinement method	Full-matrix least-squares on *F*
Parameters refined	477
Weighting scheme	Chebychev 3-term polynomial

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Goodness of fit	1.0102
R	0.0785
wR	0.0713
Residual electron density (min,max) ($eÅ^{-3}$)	-0.86, 1.13

Table 2: Bond lengths (Å) for $2[BF_4]_2$

Fe(1) - C(2)	2.111(5)	C(3) - C(15)	1.516(8)
Fe(1) - C(3)	2.152(5)	C(4) - C(5)	1.443(8)
Fe(1) - C(4)	2.085(5)	C(4) - C(16)	1.514(7)
Fe(1) - C(5)	2.086(5)	C(5) - C(6)	1.410(7)
Fe(1) - C(6)	2.167(5)	C(5) - C(17)	1.522(8)
Fe(1) - C(7)	2.086(5)	C(6) - C(7)	1.419(7)
Fe(1) - C(23)	2.064(5)	C(6) - C(18)	1.515(8)
Fe(1) - C(24)	2.067(5)	C(7) - C(8)	1.516(7)
Fe(1) - C(25)	2.049(5)	C(8) - C(9)	1.419(7)
Fe(1) - C(26)	2.048(5)	C(8) - C(13)	1.424(7)
Fe(1) - C(27)	2.056(5)	C(9) - C(10)	1.430(7)
Fe(2) - C(8)	2.064(5)	C(9) - C(19)	1.518(8)
Fe(2) - C(9)	2.176(5)	C(10) - C(11)	1.437(9)
Fe(2) - C(10)	2.109(5)	C(10) - C(20)	1.502(8)
Fe(2) - C(11)	2.096(5)	C(11) - C(12)	1.411(8)
Fe(2) - C(12)	2.120(5)	C(11) - C(21)	1.525(8)
Fe(2) - C(13)	2.109(5)	C(12) - C(13)	1.398(7)
Fe(2) - C(28)	2.053(6)	C(12) - C(22)	1.536(8)
Fe(2) - C(29)	2.058(6)	C(23) - C(24)	1.428(8)
Fe(2) - C(30)	2.045(6)	C(23) - C(27)	1.406(8)
Fe(2) - C(31)	2.045(6)	C(24) - C(25)	1.419(9)
Fe(2) - C(32)	2.055(6)	C(25) - C(26)	1.413(8)
C(1) - C(2)	1.509(7)	C(26) - C(27)	1.418(8)
C(1) - C(13)	1.511(7)	C(28) - C(29)	1.383(9)
C(1) - C(14)	1.558(7)	C(28) - C(32)	1.413(10)
C(2) - C(3)	1.410(7)	C(29) - C(30)	1.396(10)
C(2) - C(7)	1.430(8)	C(30) - C(31)	1.402(10)
C(3) - C(4)	1.413(8)	C(31) - C(32)	1.419(10)
B(1) - F(1)	1.382(8)	B(1) - F(3)	1.369(9)
B(1) - F(2)	1.385(8)	B(1) - F(4)	1.375(8)
B(2) - F(5)	1.41(1)	B(2) - F(7)	1.376(8)
B(2) - F(6)	1.363(9)	B(2) - F(8)	1.355(8)

Note – H atoms have been excluded

Table 3: Bond angles (°) for $2[BF_4]_2$

C(2) - Fe(1) - C(3)	38.60(19)	C(30) - Fe(2) - C(32)	67.5(2)
C(2) - Fe(1) - C(4)	70.8(2)	C(31) - Fe(2) - C(32)	40.5(3)
C(3) - Fe(1) - C(4)	38.9(2)	C(2) - C(1) - C(13)	102.1(4)
C(2) - Fe(1) - C(5)	84.04(19)	C(2) - C(1) - C(14)	114.7(4)
C(3) - Fe(1) - C(5)	71.2(2)	C(13) - C(1) - C(14)	110.4(4)
C(4) - Fe(1) - C(5)	40.5(2)	Fe(1) - C(2) - C(1)	135.3(3)
C(2) - Fe(1) - C(6)	70.53(19)	Fe(1) - C(2) - C(3)	72.3(3)
C(3) - Fe(1) - C(6)	83.43(18)	C(1) - C(2) - C(3)	127.0(5)
C(4) - Fe(1) - C(6)	71.6(2)	Fe(1) - C(2) - C(7)	69.1(3)
C(5) - Fe(1) - C(6)	38.7(2)	C(1) - C(2) - C(7)	111.8(4)
C(2) - Fe(1) - C(7)	39.8(2)	C(3) - C(2) - C(7)	121.1(5)
C(3) - Fe(1) - C(7)	71.4(2)	Fe(1) - C(3) - C(2)	69.1(3)
C(4) - Fe(1) - C(7)	85.61(19)	Fe(1) - C(3) - C(4)	68.0(3)
C(5) - Fe(1) - C(7)	71.12(19)	C(2) - C(3) - C(4)	119.0(5)
C(6) - Fe(1) - C(7)	38.9(2)	Fe(1) - C(3) - C(15)	135.5(4)
C(2) - Fe(1) - C(23)	175.9(2)	C(2) - C(3) - C(15)	120.6(5)
C(3) - Fe(1) - C(23)	143.3(2)	C(4) - C(3) - C(15)	120.4(5)
C(4) - Fe(1) - C(23)	112.6(2)	Fe(1) - C(4) - C(3)	73.1(3)
C(5) - Fe(1) - C(23)	100.0(2)	Fe(1) - C(4) - C(5)	69.8(3)
C(6) - Fe(1) - C(23)	112.4(2)	C(3) - C(4) - C(5)	119.5(5)
C(2) - Fe(1) - C(24)	136.8(2)	Fe(1) - C(4) - C(16)	130.5(4)
C(3) - Fe(1) - C(24)	169.8(2)	C(3) - C(4) - C(16)	119.9(5)
C(4) - Fe(1) - C(24)	150.2(2)	C(5) - C(4) - C(16)	120.7(5)
C(5) - Fe(1) - C(24)	119.0(2)	Fe(1) - C(5) - C(4)	69.7(3)
C(6) - Fe(1) - C(24)	103.8(2)	Fe(1) - C(5) - C(6)	73.8(3)
C(2) - Fe(1) - C(25)	108.5(2)	C(4) - C(5) - C(6)	121.4(5)
C(3) - Fe(1) - C(25)	129.4(2)	Fe(1) - C(5) - C(17)	129.5(4)
C(4) - Fe(1) - C(25)	159.8(2)	C(4) - C(5) - C(17)	119.1(5)
C(5) - Fe(1) - C(25)	158.4(2)	C(6) - C(5) - C(17)	119.5(5)
C(6) - Fe(1) - C(25)	127.9(2)	Fe(1) - C(6) - C(5)	67.5(3)
C(2) - Fe(1) - C(26)	109.0(2)	Fe(1) - C(6) - C(7)	67.5(3)
C(3) - Fe(1) - C(26)	103.7(2)	C(5) - C(6) - C(7)	118.0(5)
C(4) - Fe(1) - C(26)	119.9(2)	Fe(1) - C(6) - C(18)	140.5(4)
C(5) - Fe(1) - C(26)	152.6(2)	C(5) - C(6) - C(18)	118.6(5)
C(6) - Fe(1) - C(26)	168.1(2)	C(7) - C(6) - C(18)	123.3(5)
C(2) - Fe(1) - C(27)	138.6(2)	Fe(1) - C(7) - C(2)	71.0(3)
C(3) - Fe(1) - C(27)	110.1(2)	Fe(1) - C(7) - C(6)	73.6(3)
C(4) - Fe(1) - C(27)	99.0(2)	C(2) - C(7) - C(6)	120.2(4)
C(5) - Fe(1) - C(27)	114.7(2)	Fe(1) - C(7) - C(8)	130.1(3)
C(6) - Fe(1) - C(27)	146.1(2)	C(2) - C(7) - C(8)	106.5(4)
C(7) - Fe(1) - C(23)	141.1(2)	C(6) - C(7) - C(8)	133.1(5)
C(7) - Fe(1) - C(24)	109.6(2)	Fe(2) - C(8) - C(7)	121.1(3)
C(23) - Fe(1) - C(24)	40.4(2)	Fe(2) - C(8) - C(9)	74.7(3)
C(7) - Fe(1) - C(25)	106.9(2)	C(7) - C(8) - C(9)	133.6(5)
C(23) - Fe(1) - C(25)	67.5(2)	Fe(2) - C(8) - C(13)	71.8(3)
C(24) - Fe(1) - C(25)	40.3(2)	C(7) - C(8) - C(13)	106.9(4)
C(7) - Fe(1) - C(26)	134.0(2)	C(9) - C(8) - C(13)	119.5(5)
C(23) - Fe(1) - C(26)	67.5(2)	Fe(2) - C(9) - C(8)	66.3(3)
C(24) - Fe(1) - C(26)	68.0(2)	Fe(2) - C(9) - C(10)	68.0(3)
C(25) - Fe(1) - C(26)	40.4(2)	C(8) - C(9) - C(10)	118.1(5)
C(7) - Fe(1) - C(27)	174.2(2)	Fe(2) - C(9) - C(19)	144.0(4)
C(23) - Fe(1) - C(27)	39.9(2)	C(8) - C(9) - C(19)	123.8(5)
C(24) - Fe(1) - C(27)	67.9(2)	C(10) - C(9) - C(19)	117.8(5)

C(25) - Fe(1) - C(27)	67.7(2)	Fe(2) - C(10) - C(9)	73.0(3)
C(26) - Fe(1) - C(27)	40.4(2)	Fe(2) - C(10) - C(11)	69.5(3)
C(8) - Fe(2) - C(9)	39.0(2)	C(9) - C(10) - C(11)	120.5(5)
C(8) - Fe(2) - C(10)	71.68(19)	Fe(2) - C(10) - C(20)	129.6(4)
C(9) - Fe(2) - C(10)	39.0(2)	C(9) - C(10) - C(20)	118.8(5)
C(8) - Fe(2) - C(11)	85.90(19)	C(11) - C(10) - C(20)	120.7(5)
C(9) - Fe(2) - C(11)	71.3(2)	Fe(2) - C(11) - C(10)	70.5(3)
C(10) - Fe(2) - C(11)	40.0(2)	Fe(2) - C(11) - C(12)	71.4(3)
C(8) - Fe(2) - C(12)	72.2(2)	C(10) - C(11) - C(12)	119.9(5)
C(9) - Fe(2) - C(12)	83.7(2)	Fe(2) - C(11) - C(21)	131.9(4)
C(10) - Fe(2) - C(12)	71.3(2)	C(10) - C(11) - C(21)	119.8(5)
C(11) - Fe(2) - C(12)	39.1(2)	C(12) - C(11) - C(21)	120.3(5)
C(8) - Fe(2) - C(13)	39.9(2)	Fe(2) - C(12) - C(11)	69.5(3)
C(9) - Fe(2) - C(13)	69.92(19)	Fe(2) - C(12) - C(13)	70.3(3)
C(10) - Fe(2) - C(13)	83.5(2)	C(11) - C(12) - C(13)	119.1(5)
C(11) - Fe(2) - C(13)	70.3(2)	Fe(2) - C(12) - C(22)	130.8(4)
C(12) - Fe(2) - C(13)	38.6(2)	C(11) - C(12) - C(22)	121.2(5)
C(8) - Fe(2) - C(28)	139.3(3)	C(13) - C(12) - C(22)	119.7(5)
C(9) - Fe(2) - C(28)	113.6(2)	Fe(2) - C(13) - C(1)	134.6(3)
C(10) - Fe(2) - C(28)	103.4(2)	Fe(2) - C(13) - C(8)	68.4(3)
C(11) - Fe(2) - C(28)	116.8(2)	C(1) - C(13) - C(8)	111.2(4)
C(12) - Fe(2) - C(28)	146.3(3)	Fe(2) - C(13) - C(12)	71.1(3)
C(8) - Fe(2) - C(29)	108.6(2)	C(1) - C(13) - C(12)	127.0(5)
C(9) - Fe(2) - C(29)	106.3(2)	C(8) - C(13) - C(12)	121.7(5)
C(10) - Fe(2) - C(29)	123.3(3)	Fe(1) - C(23) - C(24)	69.9(3)
C(11) - Fe(2) - C(29)	154.2(3)	Fe(1) - C(23) - C(27)	69.7(3)
C(12) - Fe(2) - C(29)	165.1(3)	C(24) - C(23) - C(27)	108.6(5)
C(8) - Fe(2) - C(30)	105.4(2)	Fe(1) - C(24) - C(23)	69.7(3)
C(9) - Fe(2) - C(30)	129.3(2)	Fe(1) - C(24) - C(25)	69.1(3)
C(10) - Fe(2) - C(30)	162.1(3)	C(23) - C(24) - C(25)	106.8(5)
C(11) - Fe(2) - C(30)	157.6(3)	Fe(1) - C(25) - C(24)	70.5(3)
C(12) - Fe(2) - C(30)	125.4(3)	Fe(1) - C(25) - C(26)	69.8(3)
C(8) - Fe(2) - C(31)	132.9(2)	C(24) - C(25) - C(26)	108.7(5)
C(9) - Fe(2) - C(31)	168.9(2)	Fe(1) - C(26) - C(25)	69.8(3)
C(10) - Fe(2) - C(31)	152.0(2)	Fe(1) - C(26) - C(27)	70.1(3)
C(11) - Fe(2) - C(31)	118.6(3)	C(25) - C(26) - C(27)	107.8(5)
C(12) - Fe(2) - C(31)	101.1(2)	Fe(1) - C(27) - C(23)	70.4(3)
C(8) - Fe(2) - C(32)	172.7(2)	Fe(1) - C(27) - C(26)	69.5(3)
C(9) - Fe(2) - C(32)	146.7(3)	C(23) - C(27) - C(26)	108.0(5)
C(10) - Fe(2) - C(32)	115.5(2)	Fe(2) - C(28) - C(29)	70.5(4)
C(11) - Fe(2) - C(32)	100.4(2)	Fe(2) - C(28) - C(32)	69.9(3)
C(12) - Fe(2) - C(32)	110.5(3)	C(29) - C(28) - C(32)	108.5(6)
C(13) - Fe(2) - C(28)	172.5(2)	Fe(2) - C(29) - C(28)	70.2(4)
C(13) - Fe(2) - C(29)	134.1(2)	Fe(2) - C(29) - C(30)	69.6(4)
C(28) - Fe(2) - C(29)	39.3(3)	C(28) - C(29) - C(30)	108.5(6)
C(13) - Fe(2) - C(30)	105.8(2)	Fe(2) - C(30) - C(29)	70.6(3)
C(28) - Fe(2) - C(30)	66.8(3)	Fe(2) - C(30) - C(31)	70.0(3)
C(29) - Fe(2) - C(30)	39.8(3)	C(29) - C(30) - C(31)	108.3(5)
C(13) - Fe(2) - C(31)	107.7(2)	Fe(2) - C(31) - C(30)	69.9(3)
C(28) - Fe(2) - C(31)	67.5(3)	Fe(2) - C(31) - C(32)	70.1(3)
C(29) - Fe(2) - C(31)	67.1(3)	C(30) - C(31) - C(32)	107.6(6)
C(30) - Fe(2) - C(31)	40.1(3)	Fe(2) - C(32) - C(28)	69.8(3)
C(13) - Fe(2) - C(32)	139.1(3)	Fe(2) - C(32) - C(31)	69.4(3)

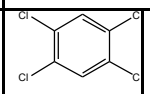
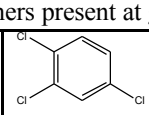
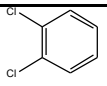
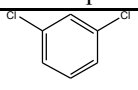
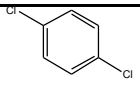
C(28) - Fe(2) - C(32)	40.2(3)	C(28) - C(32) - C(31)	107.0(6)
C(29) - Fe(2) - C(32)	67.0(3)		
F(1) - B(1) - F(2)	109.2(5)	F(1) - B(1) - F(4)	109.5(6)
F(1) - B(1) - F(3)	109.5(5)	F(2) - B(1) - F(4)	109.1(5)
F(2) - B(1) - F(3)	109.8(6)	F(3) - B(1) - F(4)	109.7(6)
F(5) - B(2) - F(6)	108.5(7)	F(5) - B(2) - F(8)	110.3(6)
F(5) - B(2) - F(7)	107.4(5)	F(6) - B(2) - F(8)	110.5(6)
F(6) - B(2) - F(7)	108.5(6)	F(7) - B(2) - F(8)	111.4(7)

Note – H atoms have been excluded

Table 4: Yields of biphenyl from dechlorination of PCBs with pyridine base

Catalyst/conditions		Time (hours)	Yield (%)
1$[PF_6]_2$	Light	4	29.7
		24	35.0
	Dark	4	35.6
		24	39.1
2$[PF_6]_2$	Light	4	30.5
		24	45.6
	Dark	4	31.3
		24	49.8
Cp_2TiCl_2	Light	4	19.9
		24	55.7

Table 5: Percentage conversion from dechlorination of 1,2,4,5-tetrachlorobenzene at various times with pyridine base, tests run in darkness

		Isomers present at given reaction time expressed as a % of detected material						
Catalyst	Time (hours)							
1$[PF_6]_2$	1	100	-	-	-	-	-	-
	2	100	-	-	-	-	-	-
	4	100	-	-	-	-	-	-
	24	100	-	-	-	-	-	-
2$[PF_6]_2$	1	100	-	-	-	-	-	-
	2	-	64.8	16.0	-	18.9	-	-
	4	-	-	19.5	-	22.0	58.5	-
	24	-	-	-	-	-	84.7	14.1